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Emission Spectra and Kinetics of Copolymer Films of Styrene and 2,3,4,5,6-Pentafluorostyrene

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ABSTRACT: The temperature-dependent steady-state emission spectra and fluorescence kinetics of copolymer films of styrene and 2,3,4,5,6-pentafluorostyrene are reported. The polystyrene excimer emission is efficiently quenched in the presence of relatively small amounts of the pentafluorophenyl quencher in spite of the fact that direct energy transfer from the excimer to the quencher chromophores is not possible. The quenching of the polystyrene excimer emission at room temperature and of the polystyrene monomer emission at 13 K is attributed to the interception of the migrating monomer excitation by the quencher. The data suggest that this quenching mechanism is independent of temperature.

1. Introduction

The photophysics of poly(vinyl aromatics)[1-5] such as polystyrene, poly(vinylnaphthalene), and poly(vinylcarbazole) have been the focus of much research. A principal goal of this research has been to understand the mechanisms of electronic energy transfer of vital importance to the photostability of synthetic polymers[6] as well as the light harvesting function of naturally occurring photosynthetic systems.[7] One strategem for studying electronic energy transfer in poly(vinyl aromatics) has been to incorporate an extrinsic trap in the polymer.[8-14] One common feature of these studies is that the absorption spectrum of the trap overlaps the emission spectrum of the excimer of the poly(vinyl aromatic). This introduces complexity into the energy-transfer analysis since many mechanisms of electronic energy transfer are, in principle, possible including dipole–dipole,[1,15,16] radiative,[1] and Dexter-type[1,17] transfer. Moreover, the extrinsic trap has been invariably of a significantly different structure from that of the poly(vinyl aromatic) pendant units. This structural dissimilarity raises concerns regarding the homogeneity of the dispersion of the extrinsic traps in the copolymers.[14,18]

We recently reported on the photophysics of pure poly(2,3,4,5,6-pentafluorostyrene),[19] the ring-perfluorinated analogue of polystyrene. The results of a study of copolymers of styrene and 2,3,4,5,6-pentafluorostyrene (PFS) are reported here. On the basis of the other study,[19] upon excitation the polymerized PFS chromophore undergoes a rapid structural distortion to an emissive state of lower energy than the first excited state of polystyrene and therefore meets the general criterion of a trap. Furthermore, the pentafluorophenyl groups provide extrinsic traps which are structurally similar to the phenyl units of polystyrene. Additionally, the absorption spectrum of polymerized PFS chromophores does not overlap the emission spectrum of the polystyrene excimer. This reduces the number of possible mechanisms of energy transfer in these copolymers. It is these rather unique aspects of the ring-perfluorinated chromophores which make these copolymers attractive systems in which to investigate electronic energy migration processes in polystyrene.

2. Methods

The structure of a copolymer of styrene and 2,3,4,5,6-pentafluorostyrene is shown in Figure 1. The synthesis of the copolymers of 2,3,4,5,6-pentafluorostyrene and styrene was carried out as follows: The 2,3,4,5,6-pentafluorostyrene was obtained from PCR Specialty Chemicals. This monomer was purified by washing with 10% sodium hydroxide and water, drying, and distilling. Styrene was dried and vacuum-distilled twice prior to use. Mixtures of a free-radical initiator (AIBN), styrene, and 2,3,4,5,6-pentafluorostyrene was made up in desired concentration ratios, placed in Pyrex tubes, deaerated by bubbling in argon, and polymerized in a water bath. The resulting white, solid copolymer was extracted with methanol in a Soxhlet column for 168 h and then analyzed by HPLC for unreacted monomer. Extraction was continued until no free styrene or 2,3,4,5,6-pentafluorostyrene could be detected. The resulting polymer was reprecipitated twice from methylene chloride solutions into methanol. The molecular weight of each polymer sample was determined by HPLC (methylene chloride as solvent) employing a set of four ultramicro Styragel molecular exclusion columns (10-, 10^2-, 10^3-, and 10^4-Å pore size), using narrow molecular weight polystyrene as the calibration standard. The films were spin-cast from ethyl acetate solutions and were typically 50–100 μm thick. The copolymers were dried exhaustively in a vacuum oven for several days at 50 °C. The compositions of the samples investigated here are given in Table I. The composition of each copolymer is based upon the relative amounts of styrene and ring-perfluorinated styrene used during the synthesis. Throughout this paper a copolymer whose 2,3,4,5,6-pentafluorostyrene mole percent content is x will be referred to as x%-PFS/PS.

Spectrophotometric grade solvents were used throughout this study. Additionally, solvents were passed through a short column of activated alumina (MCB, 80–200 mesh) prior to use.

Steady-state emission spectra were obtained with a spectrofluorimeter (Spex Fluorolog 2, Model 212) equipped with double grating emission and excitation monochromators, a high-pressure xenon lamp (450 W) for excitation, a quantum counter (rhodamine B as scintillator) to monitor the excitation beam intensity, and a photomultiplier tube (Hamamatsu R928-P) in a water-cooled housing operated in photon-counting mode to monitor the emission intensity. The linear reciprocal dispersion of the instrument is 1.8 nm/mm. The excitation wavelength used in these experiments was 255 nm with a 1.8-nm bandwidth. The

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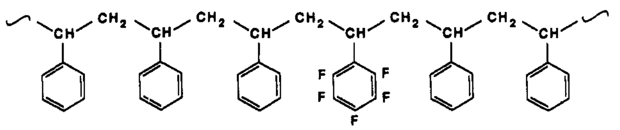

Figure 1. Structure of copolymer of styrene and 2,3,4,5,6-pentafluorostyrene. No particular conformation nor tacticity is implied.

Table I
Composition of PFS/PS Copolymers Investigated

mol % PFS	PFS molarity	M_w ($\times 10^{-3}$)	M_n ($\times 10^{-3}$)	M_w/M_n
0	0	573	271	2.12
0.0107	0.00108	598	271	2.21
0.107	0.0108	587	277	2.12
1.08	0.109	570	268	2.12
5.62	0.567	566	268	2.11

emission was collected at an angle of 22° relative to the excitation axis. Nonfluorescing filters (Schott KV) were used to eliminate interference of higher order of either the scattered excitation wavelength or shorter wavelength emission as needed. Each spectrum was corrected for fluctuations in the excitation intensity as well as the wavelength dependence of the detector response. These wavelength correction factors were obtained with a secondary standard lamp (Optronics 200W tungsten–halogen) powered by a precision current source (Optronics Model 65). The method of temperature variation of the samples has been described in detail.[19]

Fluorescence decay measurements were obtained with a picosecond laser system.[20] Briefly, the fourth harmonic pulse (λ = 266 nm, Δt = 8 ps) of an Nd^{3+}:glass laser system was focused (quartz lens, 5-in. focal length) onto the sample positioned at an angle of ≈60° with respect to the incident excitation axis. The emission was collected at 90° with respect to the incident excitation axis with a quartz lens (2-in. diameter, *f*:1) and relayed to a fast biplanar photodiode (ITT F4000) through appropriate filters to remove any scattered laser light. The resulting signal was monitored by a 500-MHz bandwidth oscilloscope (Tektronix 7904 with Tektronix 7A19 vertical amplifier and 7B85 time base). Oscilloscope traces were photographed with a Tektronix-125 (*f*: 1.5) camera and Polaroid 612 film (ASA 20000). Xerographic transparencies of the oscilloscope traces were made from the photographs. These transparencies were enlarged to a convenient size for subsequent digitizing with a microcomputer (HP 87) and plotter (HP 7470A).

It was assumed that the fluorescence of the samples decayed exponentially. The experimentally obtained decay profile could thus be expressed in the functional form[21,22]

$$I(t) = Ae^{-t/\tau}\int_{-\infty}^{t} S(t')e^{t'/\tau}\,\mathrm{d}t' \qquad (1)$$

in which $I(t)$ is the fluorescence intensity as a function of time, and A and τ, the fluorescence lifetime, are parameters. $S(t)$ is the intensity of a scattered laser pulse as a function of time and was obtained experimentally by scattering the exciting pulse off a dilute solution of nondairy coffee creamer in water. $S(t)$ was obtained by using the same optical configuration as used to obtain $I(t)$. A linear least-squares fit of the Taylor series expansion to first order in the two parameters[23] of the above function, which is a convolution of the detector response to the scattered laser pulse and the fluorescence of the sample, to a decay profile was then done iteratively until the minimum in the root-mean-square value was obtained. Since there was some uncertainty in the position of $t = 0$ (the time position corresponding to the peak of the excitation pulse) in $I(t)$, the relative time between $I(t)$ and $S(t)$ was varied over a range of ~300 ps during the fitting process.

3. Results

3.1. Steady-State Emission Spectra. The room temperature emission spectra of the PFS/PS copolymer films are shown in Figure 2. The spectra are marked by a dramatic decrease in the polystyrene excimer emission intensity (λ_{max} ~ 325 nm) with increasing PFS content.

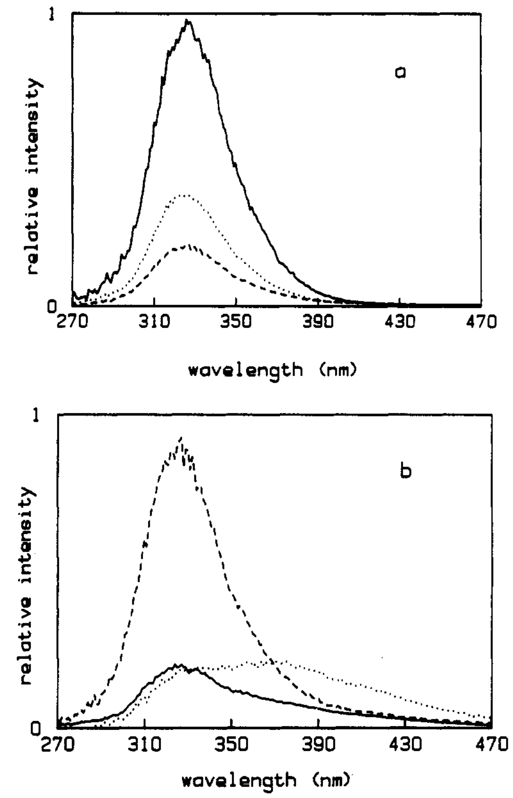

Figure 2. Room temperature emission spectra (λ_{ex} = 255 nm) of x%-PFS/PS copolymer films (a) where x = 0 (—), 0.0107 (···), and 0.107 (- - -) and (b) where x = 0.107 (- - -), 1.08 (—), and 5.62 (···).

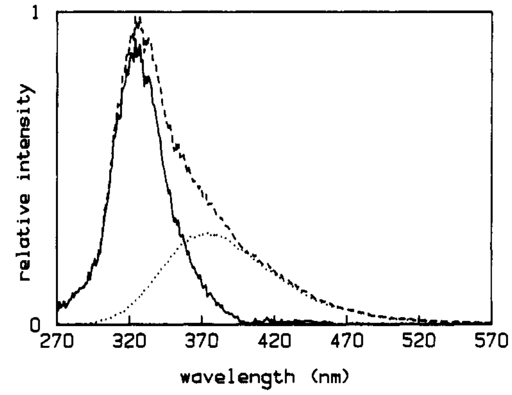

Figure 3. Room temperature emission spectrum (λ_{ex} = 255 nm) due to the polystyrene excimer only (—) in the 1.08%-PFS/PS copolymer film is the difference spectrum of the copolymer emission spectrum (- - -) and the tail-matched (430–500 nm) spectrum of neat PFS film (···). See text for details.

Close scrutiny of the spectra reveals a concomitant increase in the emission intensity near 380 nm associated with the PFS chromophore.

To quantify the degree of quenching of the polystyrene excimer emission intensity in these copolymer films as a function of the PFS content, it is necessary to extract that portion of the spectrum for each of the copolymers due to the polystyrene chromophores only. (Throughout this paper we will refer to the phenyl chromophores of the copolymers as the polystyrene chromophores and the emission associated with these chromophores as excimer or monomer emission.) The following procedure was used to do this for the 1.08%-PFS/PS copolymer film spectrum. Examination of Figure 3 will aid in this discussion. It was assumed that the emission intensity of the PFS/PS copolymer films at wavelengths greater than 430 nm was solely ascribable to the PFS chromophores. This is based

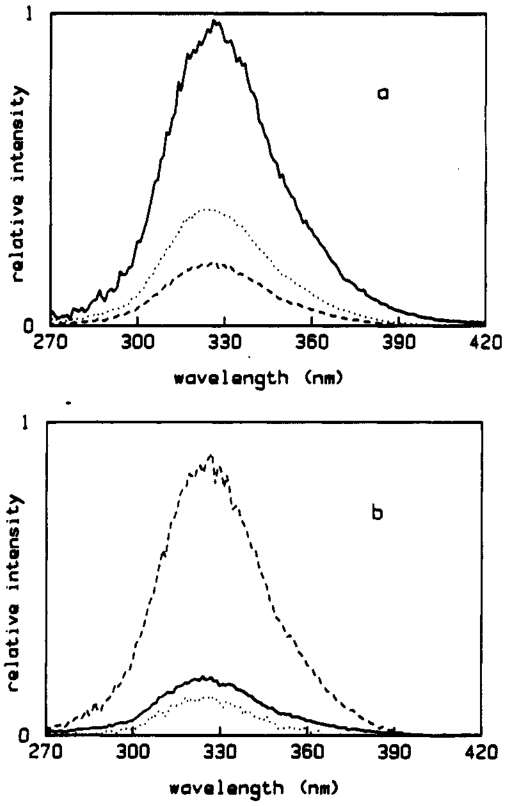

Figure 4. Room temperature difference emission spectra due to the polystyrene chromophores of x%-PFS/PS copolymer films after subtracting the PFS emission (a) where x = 0 (▬), 0.0107 (···), and 0.107 (- - -) and (b) where x = 0.107 (- - -), 1.08 (—), and 5.62 (···). (λ_{ex} = 255 nm.)

Table II
Relative Excimer Emission Intensities of PFS/PS Copolymer Films at Room Temperature

mol % PFS	I	S	I_c[a]
0	1	1.00	1
0.0107	0.40	1.00	0.40 ± 0.01
0.107	0.23	1.00	0.23 ± 0.01
1.08	0.052	1.02	0.053 ± 0.01
5.62	0.029	1.11	0.032 ± 0.01

[a] I_c is the relative intensity obtained by multiplying the intensity value I by the screening correction factor S. See text.

on the fact that the room temperature emission of neat polystyrene film[1,14] is negligible in this region, while the emission spectrum of neat PFS film[19] exhibits significant intensity extending to about 500 nm. The room temperature emission spectrum of neat PFS film was then scaled until the sum of the squares of the differences of the intensity values over the wavelength range 430–500 nm between it and the 1.08%-PFS/PS emission spectrum was minimized. The resulting PFS emission spectrum was then subtracted from the 1.08%-PFS/PS copolymer film spectrum to yield the emission spectrum of the phenyl chromophores only in the copolymer. This procedure was carried out on all of the copolymer film spectra, and the resulting spectra are shown in Figure 4. These spectra more accurately reflect the degree of quenching of the excimer emission intensity due to the presence of the PFS chromophores. The relative integrated intensity of the excimer emission (300–400 nm), normalized to the pure polystyrene film value, for each of these films at room temperature is shown in Table II.

One mechanism resulting in decreasing excimer emission with increasing PFS concentration is competitive direct absorption by the PFS chromophores of the incident 255-nm photons. Since PFS absorbs at the excitation wavelength, the excimer emission decreases with increasing PFS concentration due to an effective attenuated source. The emission intensity of each film can be normalized to a constant excitation intensity by a corresponding screening factor S, where

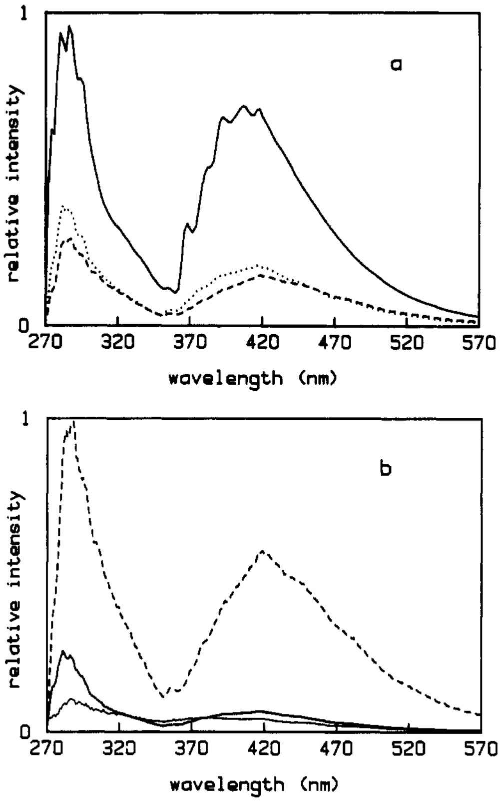

Figure 5. Emission spectra at 13 K (λ_{ex} = 255 nm) of x%-PFS/PS copolymer films (a) where x = 0 (▬), 0.0107 (···), and 0.107 (- - -) and (b) where x = 0.107 (- - -), 1.08 (▬), and 5.62 (—).

$$S = (\mathrm{OD_{PFS}} + \mathrm{OD_{PS}})/\mathrm{OD_{PS}} \qquad (2)$$

$$S = [\epsilon_{\mathrm{PFS}}(255\ \mathrm{nm})C_{\mathrm{PFS}} + \epsilon_{\mathrm{PS}}(255\ \mathrm{nm})C_{\mathrm{PS}}]/\epsilon_{\mathrm{PS}}(255\ \mathrm{nm})C_{\mathrm{PS}}$$

in which $\epsilon_{\mathrm{PFS}}(255\ \mathrm{nm}) = 294\ \mathrm{cm^{-1}\ M^{-1}}$ and $\epsilon_{\mathrm{PS}}(255\ \mathrm{nm}) = 172\ \mathrm{cm^{-1}\ M^{-1}}$. These extinction coefficients are the values obtained for neat PFS in ethyl acetate and neat PS in cyclohexane. These screening correction factors are given in Table II. The screening factors are relatively small except for the 5.62%-PFS/PS, and thus any uncertainty due to the use of the solution absorption values should not appreciably affect the overall results. The integrated excimer emission intensity values of the PFS/PS copolymer films were multiplied by the corresponding screening correction factors to yield values that more accurately reflect the degree of quenching of the excimer emission by nonradiative processes. These corrected relative integrated intensity values are given in Table II.

The emission spectra of the copolymer films at 13 K are shown in Figure 5. The polystyrene monomer fluorescence (λ_{max} ~ 285 nm) and phosphorescence (λ_{max} ~ 410 nm) are the most intense bands in the spectra. Additionally, the shoulder near 330 nm is due to the polystyrene excimer. As the PFS content increases, the spectra show evidence of increasing PFS fluorescence (λ_{max} ~ 380 nm) and phosphorescence[19] (λ_{max} ~ 450 nm). Although the integrated emission intensity decreases with increasing PFS content, the overlap of these emission bands results

Table III
Relative Polystyrene Monomer Fluorescence Intensities of PFS/PS Copolymer Films at 13 K

mol % PFS	I	S	I_c[a]
0	1	1.00	1
0.0107	0.38	1.00	0.38 ± 0.01
0.107	0.28	1.00	0.28 ± 0.01
1.08	0.060	1.02	0.061 ± 0.01
5.62	0.026	1.11	0.029 ± 0.01

[a] I_c is the relative intensity obtained by multiplying the intensity value I by the screening correction factor S. See text.

Table IV
Room Temperature Fluorescence Lifetimes of PFS/PS Copolymer Films

mol % PFS	τ, ns	mol % PFS	τ, ns
0	21.0 ± 1.4	0.107	21.4 ± 2.0
0.0107	22.0 ± 2.0		

in a nonuniform change in intensity as a function of wavelength. This nonuniformity is most evident in the region where the polystyrene monomer and excimer fluorescences overlap the PFS fluorescence and the region where the polystyrene and PFS phosphorescences overlap. However, in the region where the polystyrene monomer emission is most intense ($\lambda_{max} \sim 285$ nm), the emission of the PFS chromophores[19] is weak as is that of the polystyrene excimer. In this wavelength region the spectra show a monotonic decrease in the polystyrene monomer emission intensity with increasing PFS content. The relative integrated (280–290 nm) monomer fluorescence intensities at 13 K of these copolymer films are shown in Table III. As with the room temperature data, these values are multiplied by the appropriate screening correction value S to obtain the relative integrated emission intensities which reflect the degree of nonradiative quenching of the polystyrene monomer due to the PFS chromophores. These resultant values are shown in Table III. The relatively small values of S suggest that the expected uncertainty in the overall results due to the use of the room temperature solution absorption values rather than the low-temperature solid film values in the calculation of the S values should be minimal. Since the integration was not carried out over the entire monomer fluorescence band at low temperature (congestion of the spectra made it impossible to separate out the entire monomer fluorescence), the correlation of the reported relative integrated monomer emission intensities and the actual values is more uncertain than in the case of the excimer emission at room temperature. (See Tables II and III. The uncertainties in the corrected intensities reported in these tables, while correct in terms of the measurements, do not include these considerations.)

3.2. Fluorescence Kinetics. The room temperature fluorescence decay profiles of neat polystyrene film and the 0.107%-PFS/PS copolymer film are shown in Figure 6. A linear least-squares fit of an exponentially decaying convolution integral (eq 1) to the data yielded fluorescence decay times of 21.0 ± 1.4 and 22.0 ± 2.0 ns, respectively. The best fit of the function to the data is also shown in Figure 6. The fluorescence decay lifetime of the 0.0107%-PFS/PS copolymer was obtained as well and found to be 21.4 ± 2.0 ns. These values are in agreement with previously reported values of the polystyrene excimer fluorescence lifetime in room temperature films.[24] The emission of the PFS chromophores in the 0.0107%- and 0.107%-PFS/PS copolymers is relatively weak compared to that of the excimer (see Figure 2). We can therefore conclude that these lifetimes are associated with the polystyrene excimer in these copolymers. These results are summarized in Table IV. It was not possible to obtain the decay kinetics of the polystyrene excimer in the films of greater PFS content due to the relatively weak excimer fluorescence intensity (see Table II).

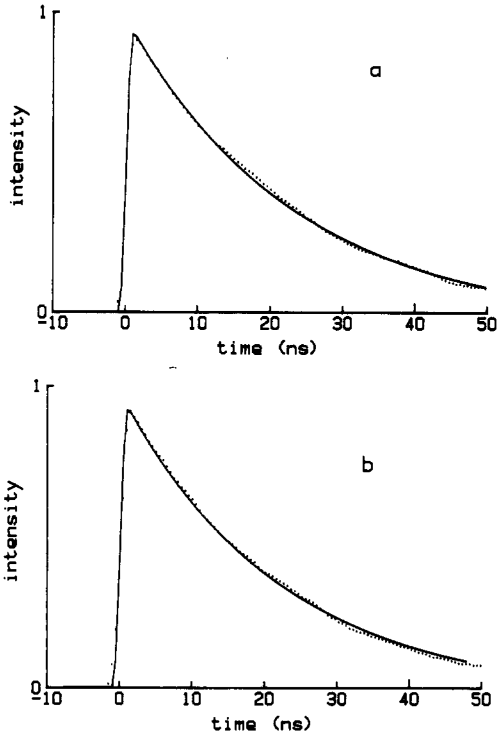

Figure 6. (a) Fluorescence decay profile of neat polystyrene film at room temperature (λ_{ex} = 266 nm). The solid line is the best fit of the single-exponential decay convolution integral (see text) to the data points. (b) Fluorescence decay profile of 0.107%-PFS/PS copolymer film at room temperature (λ_{ex} = 266 nm). The solid line is the best fit of the single-exponential decay convolution integral (see text) to the data points.

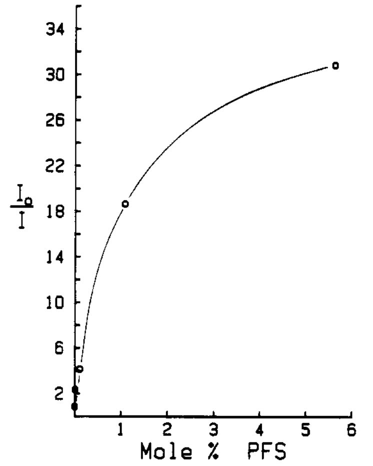

Figure 7. Dependence of the ratio of the polystyrene excimer fluorescence intensity, I_0, to the corrected excimer fluorescence intensity, I, on the content of the PFS chromophore in the copolymer film at room temperature (O).

4. Discussion

It is illustrative to plot (Figure 7) the ratio of the room temperature corrected emission intensity (Table II) of the excimer in pure polystyrene film, I_0, to the corresponding value of each of the PFS/PS copolymers, I, as a function of the PFS content. Clearly, the presence of relatively small amounts of PFS results in significant quenching of the excimer emission. The fluorescence kinetics data

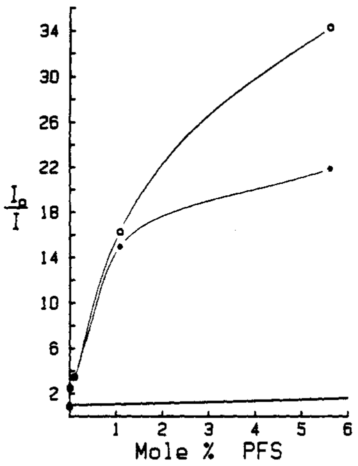

Figure 8. Dependence of the ratio of the polystyrene monomer fluorescence intensity, I_0, to the corrected monomer fluorescence intensity, I, on the content of the PFS chromophore in the copolymer films at 13 K (○). The lowest solid line is the calculated quenching efficiency due to long-range dipole–dipole energy transfer from the monomer to PFS at 13 K. The asterisks are indicative of precursor quenching at 13 K. See text.

(Table IV) indicate that the excimer lifetime in the copolymers remains unchanged from the neat polystyrene film value until at least 0.107% PFS is present, at which point the ratio of $I_0/I \sim 4$. This suggests that the excimer itself is not being directly quenched, but rather the excited-state precursor to excimer formation is being quenched. This is consistent with the fact that since the excimer emission and the PFS absorption do not overlap, direct energy transfer from the excimer to the PFS chromophore is not possible. To our knowledge this is the first report of quenching of the excimer emission in a poly(vinyl aromatic) polymer system that contains a trap chromophore that cannot act as a direct acceptor of the excimer emission by either radiative or nonradiative energy transfer. This finding of precursor quenching of the excimer in polystyrene validates the notion that excimers are formed as the result of electronic excitation migrating in polystyrene to an excimer-forming site. These data are consistent with the hypothesis that the PFS chromophore traps this mobile excitation and thus inhibits the formation of the excimers. Therefore, the data points in Figure 7 are indicative of the degree of precursor quenching.

The ratio of the corrected emission intensity (Table III) of the monomer in pure polystyrene film, I_0, to the corresponding value for each of the PFS/PS copolymers, I, as a function of the PFS content at 13 K is plotted in Figure 8. Since the polystyrene monomer fluorescence overlaps with the PFS absorption, long-range dipole–dipole energy transfer may occur from the monomer to the PFS chromophores. To determine the degree of quenching due to this mechanism, the Foerster critical radius was calculated from the PFS absorption spectrum and polystyrene emission spectrum by using the following equation:[25]

$$R_0^6 = \frac{9000\kappa^2 \ln 10\,\phi_D}{128\pi^5 n^4 N}\int_0^\infty F_D(\bar{\nu})\epsilon_A(\bar{\nu})\frac{d\bar{\nu}}{\bar{\nu}^4} \qquad (3)$$

In this equation, ϕ_D is the quantum yield of emission of the polystyrene monomer[26] in the absence of PFS (ϕ_D = 0.17 ± 0.08), n is the index of refraction of the film and is assumed to be the same as that of neat polystyrene[27] (n = 1.592), N is Avogadro's number, $F_D(\bar{\nu})$ is the emission spectrum of the polystyrene monomer normalized such that $\int F_D(\bar{\nu})\,d\bar{\nu} = 1$, and $\epsilon_A(\bar{\nu})$ is the molar extinction coefficient of the PFS chromophores as a function of $\bar{\nu}$. In the solid state the orientation factor κ^2 is usually taken to be 0.475 such as would be expected for a random distribution of the transition dipole orientations of the donor and acceptor molecules. The resulting Foerster critical radius value of R_0 = 6 Å is the separation distance between the donor, the polystyrene monomer, and the acceptor, the PFS chromophore, at which the probability of Foerster (dipole–dipole) electronic energy transfer is 0.5. This value was subsequently utilized to determine the degree of quenching of the monomer steady-state emission in the PFS/PS copolymers which is due solely to dipole–dipole electronic energy transfer. The equations[28,29] that relate these quantities are

$$f = \pi^{1/2}\gamma \exp(\gamma^2)[1 - \mathrm{erf}(\gamma)] \qquad f = (\phi_0 - \phi)/\phi_0$$
$$\gamma = C/C_0 \qquad C_0 = 3000/(2\pi^{3/2}NR_0^{\,3}) \qquad (4)$$

in which ϕ_0 and ϕ are the emission quantum yields of the monomer donor in the absence and presence of the PFS acceptor, respectively, of concentration C; γ is termed the quenching efficiency; and N is again Avogadro's number. Equation 4 was used to obtain the lowest curve of Figure 8. The large difference between this curve and the experimental points suggests that precursor quenching of the monomer is also prevalent in these copolymers at 13 K. This further validates the proposition that electronic energy migration is significant in these copolymers. The degree of precursor quenching was obtained by dividing the experimentally obtained values by the corresponding values from the lowest curve. The resulting data points are shown in Figure 8 as well.

Examination of the precursor quenching curves in Figures 7 and 8 indicates that the precursor quenching efficiency is the same within experimental uncertainty at room temperature and 13 K for copolymer films containing less than about 1% PFS. Assuming that the precursor quenching is the result of energy migration followed by a single-step dipole–dipole energy transfer to a trap, this suggests that energy migration in these polymers is also independent of temperature since the dipole–dipole energy-transfer rate is independent of temperature. (This argument assumes that the pure radiative rate constant of the donor, the absorption spectrum of the acceptor, and the shape of the emission spectrum of the donor are approximately temperature independent.) Temperature-independent energy migration is expected if the migration consists of a series of single-step dipole–dipole energy transfers from phenyl unit to phenyl unit. The precursor quenching data for the 5.62%-PFS/PS copolymer film at 13 K and room temperature appears significantly different. However, these are the experimental data of the greatest uncertainty. In particular, we suspect that we have understated the quenching efficiency of the monomer fluorescence at 13 K in this copolymer by assuming that only the monomer fluoresces in the integrated region 280–290 nm. This assumption may be particularly invalid when the monomer emission is very weak and the PFS emission relatively strong as is the case in this copolymer. Such an understatement of the quenching efficiency would result in the precursor quenching data point of Figure 8 being lower than the corresponding point at room temperature.

We have reported on related studies[1,14,26,30] of copolymers of styrene and 2-(2′-hydroxy-5′-vinylphenyl)benzotriazole (HPB/PS). Comparison of the quenching of the polystyrene emission in the PFS/PS copolymer films (Figures 7 and 8) with the quenching in the HPB/PS copolymer films shows that the quenching efficiency is similar in the two sets of films. In both cases, the precursor quenching efficiency increases rapidly with increasing quencher concentration at relatively low concentrations of the quencher. The precursor quenching efficiency then flattens out with increasing quencher concentration. This flat plateau region occurs at a greater I_0/I value for the PFS/PS copolymers. That is, while we estimated that approximately 15–20% of the excimer emission in the HPB/PS copolymers could not be quenched by precursor quenching,[14] it appears that for the PFS/PS copolymers that perhaps less than 5% of the excimer emission cannot be quenched by precursor quenching. This difference could well be the result of a more uniformly homogeneous distribution of the PFS chromophores than of the HPB chromophores in the respective copolymers.

5. Summary

The data suggest that electronic energy migration is significant in these PFS/PS copolymer films at room temperature and 13 K. The polystyrene emission intensity is efficiently quenched by trapping of the mobile excitation by the PFS chromophores. The trapping of the mobile excitation and, thus, the energy migration appear to be independent of temperature. That is, there is not significant barrier to energy migration in these copolymer films even at 15 K. The PFS chromophores are efficient traps due to the rapid excited-state geometry change which results in a lowering of their excited-state energy.

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References and Notes

(1) O'Connor, D. B.; Scott, G. W. In *Lasers in Polymer Science and Technology: Applications*; Fouassier, J. P., Rabek, J., Eds.; CRC Uniscience: Boca Raton, FL, 1990; Vol. I, Chapter 8.

(2) Guillet, J. *Polymer Photophysics and Photochemistry: An Introduction to the Study of Photoprocesses in Macromolecules*; Cambridge University Press: Cambridge, U.K., 1985.

(3) Phillips, D., Ed. *Polymer Photophysics: Luminescence, Energy Migration and Molecular Motion in Synthetic Polymers*; Chapman and Hall: London, 1985.

(4) Kloepffer, W. In *Aromatic polymers in dilute solution. Electronic energy transfer and trapping*; ACS Symposium Series 358; American Chemical Society: Washington, DC, 1987; p 301.

(5) Fredrickson, G. H.; Andersen, H. C.; Frank, C. W. *Macromolecules* **1984**, *17*, 54.

(6) Ranby, B.; Rabek, J. F. In *Photodegradation, Photooxidation, and Photostabilization of Polymers: Principles and Applications*; Wiley: New York, 1975.

(7) Clayton, R. K. *Photosynthesis: Physical Mechanisms and Chemical Patterns*; Cambridge University Press: Cambridge, U.K., 1980.

(8) Phillips, D.; Roberts, A. J.; Soutar, I. *Macromolecules* **1983**, *16*, 1593.

(9) Basile, L. J.; Weinreb, A. *J. Chem. Phys.* **1960**, *33*, 1028.

(10) Johnson, G. E. *Macromolecules* **1980**, *13*, 145.

(11) North, A. M.; Ross, D. A.; Treadway, M. F. *Eur. Polym. J.* **1974**, *10*, 411.

(12) Kloepffer, W. *J. Chem. Phys.* **1969**, *50*, 2337.

(13) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3737.

(14) Coulter, D. R.; Gupta, A.; Yavrouian, A.; Scott, G. W.; O'Connor, D.; Vogl, O.; Li, S.-C. *Macromolecules* **1986**, *19*, 1227.

(15) Foerster, Th. *Ann. Phys.* **1948**, *2*, 55.

(16) Foerster, Th. *Z. Naturforsch.* **1949**, *49*, 321.

(17) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.

(18) Reference 2, pp 237–240.

(19) O'Connor, D. B.; Scott, G. W.; Coulter, D. R.; Miskowski, V. M.; Yavrouian, A. *J. Phys. Chem.* **1990**, *94*, 6495.

(20) Talley, L. D. Picosecond kinetics of electronic excited states of aromatic ketones and diazanaphthalenes. Ph.D. Thesis, University of California, Riverside, 1979.

(21) Haug, A.; Kohler, B. E.; Priestley, E. B.; Robinson, G. W. *Rev. Sci. Instrum.* **1969**, *40*, 1439.

(22) Huston, A. L.; Scott, G. W.; Gupta, A. *J. Chem. Phys.* **1982**, *76*, 4978.

(23) Bevington, P. R. In *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969; Chapter 11, p 232.

(24) Gupta, M. D.; Gupta, A.; Horwitz, J.; Kliger, D. *Macromolecules* **1982**, *15*, 1372.

(25) Berlman, I. B. *Energy Transfer Parameters of Aromatic Compounds*; Academic Press: New York, 1973.

(26) O'Connor, D. B. The photophysics of polystyrene and poly(2,3,4,5,6-pentafluorostyrene): Electronic energy processes in polymer films. Ph.D. Thesis, University of California, Riverside, 1990.

(27) Boundy, R. H., Boyer, R. F., Stoesser, S. M., Eds. *Styrene, Its Polymers, Copolymers, and Derivatives*; Reinhold: New York, 1952.

(28) Foerster, Th. *Discuss. Faraday Soc.* **1959**, *27*, 7.

(29) Eisenthal, K. B.; Siegals, S. *J. Chem. Phys.* **1964**, *41*, 652.

(30) O'Connor, D. B.; Scott, G. W.; Coulter, D. R.; Gupta, A.; Webb, S. P.; Yeh, S. W.; Clark, J. H. *Chem. Phys. Lett.* **1985**, *121*, 417.