424 Macromolecules 1982, 15, 424–429

# Excited-State Properties of Poly(2-vinylnaphthalene) Containing Pyrene Groups

**John S. Hargreaves and Stephen E. Webber***

*Department of Chemistry and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712.* *Received September 25, 1981*

ABSTRACT: Singlet-energy sensitization of pyrene by naphthalene has been studied in polymers of 2-vinylnaphthalene terminated by pyrene (P2VN-Py) or copolymers of 2-vinylnaphthalene and 3-vinylpyrene (P(2VN-co-3VPy)). The quantum efficiency ($\chi$) of singlet sensitization for P2VN-Py of different molecular weights is in the range 1.5–4.8% in fluid solution, 3–6% in polystyrene matrices, and 12–35% in MTHF glasses at 77 K or neat films. In general, $\chi$ decreases with increasing chain length for P2VN-Py. For P(2VN-co-3VPy) $\chi$ is significantly higher and depends only on the mole fraction of pyrene in the copolymer. The quenching of the directly excited singlet and triplet state of pyrene in these two polymers was also studied. It was found that the quenching rate of polymer-bound pyrene was essentially unchanged from that of 3-methylpyrene in the case of P2VN-Py and halved in the case of P(2VN-co-3VPy).

## I. Introduction

There have been a number of studies in recent years using fluorescence probes in macromolecules to elucidate polymer chain motions such as rotations of pendent or in-chain chromophores or the rate of end-to-end contacts. Probe molecules have been used to determine the rate of small-molecule–polymer coil reactions, especially by Hori et al.[1] Less common has been the use of fluorescence probes to assess intracoil energy transfer, with the work of Guillet and co-workers standing as the only examples known to us.[2] In this latter work it has been found that in poly(naphthylmethyl methacrylates) intracoil singlet energy transfer to terminal or intrachain anthracene traps is quite efficient, implying that significant energy migration along the chain occurs. Some poly(naphthylmethyl methacrylates) exhibit low excimer formation and hence one is led to the reasonable assumption that excimer formation greatly retards energy migration and hence sensitized fluorescence. Part of the motivation in carrying out the present studies is to characterize another polymer–trap system with properties significantly different from those of the poly(naphthylmethyl methacrylate)–anthracene systems of Guillet et al.[2] in order to establish the generalities of intrapolymer energy transfer. The systems we present here are polymers of 2-vinylnaphthalene terminated with pyrene groups (P2VN-Py) and copolymers of 2-vinylnaphthalene and 3-vinylpyrene (P(2VN-co-3VPy)). We may briefly state the following main conclusions of this study: (1) As expected the quantum efficiency of pyrene-sensitized fluorescence in P2VN-Py or P(2VN-co-3VPy) is lower than that of the system of Holden and Guillet;[2a] this is consistent with the previous estimate that the singlet migration rate in P2VN is close to zero.[3] (2) The quantum efficiency of pyrene sensitization was not very dependent on the fluid solvents that were tried but it is quite drastically altered in films of low-temperature glasses. (3) For equivalent mole fractions of pyrene, the energy transfer to the pyrene trap is much more efficient in P(2VN-co-3VPy) than P2VN-Py. Analogous observations were made by Holden and Guillet.[2a]

In addition to the studies of sensitized pyrene fluorescence summarized above, we have studied the quenching of the singlet or triplet state of directly excited pyrene ($^1$Py*, $^3$Py*). The objective of this study is to assess the "polymer effect" on the rate of small-molecule–reactive polymer site collision by comparison to a 3-methylpyrene model. The excited-state quenching rate constant for P2VN-Py was of the same order of magnitude as for 3-methylpyrene while for P(2VN-co-3VPy) we found a decrease by a factor of approximately 2. Thus for this particular polymer system there does not seem to be any evidence for "steric hindrance" that protects a polymer-bound probe. Similar results have been reported for polystyrene–anthracene copolymers in which the anthracene triplet state was quenched.[1]

## II. Experimental Section

**A. Preparation of Materials.** 2-Vinylnaphthalene was purchased from Aldrich Chemical Co. and purified by multiple sublimation under vacuum prior to polymerization. The pyrene derivatives were synthesized by Dr. L. Kwart using pyrene-3-carboxaldehyde (Aldrich Chemical Co.) as the starting material by the following procedures.

1. **3-(Bromomethyl)pyrene.** To 0.410 g of pyrene-3-carboxaldehyde in 70 mL of 2-propanol at 82 °C was added 0.07 g of sodium borohydride. After 5 min, 0.2 mL of water and 0.2 mg of activated charcoal were added, and the mix was refluxed for a further 5 min. After filtration and evaporation of the solvent under vacuum, the residue was purified via dry-column chromatography on silica gel containing 10% water, using dichloromethane. This resulted in purification of the alcohol derivative.

To a stirred solution of 108 mg of red phosphorus in 10 mL of chloroform under a nitrogen atmosphere was added 210 mg of bromine. When no red color remained, 99 mg of the alcohol was added and the mixture refluxed for several hours, after which it was poured into water and washed with dichloromethane and the water layer removed. The organic layer was washed with sodium bicarbonate solution, followed by water, and dried over $MgSO_4$. The solution was concentrated in vacuo.

After vacuum sublimation the resulting white solid was identified by mass spectral analysis as 3-(bromomethyl)pyrene.

2. **3-Vinylpyrene.** This derivative was prepared following a slight modification of the procedure of Tanikawa et al.[4] To a stirred solution of 7.7 mmol of sodium amide in 25 mL of freshly distilled anhydrous tetrahydrofuran under nitrogen was placed 8.4 mmol of methyltriphenylphosphonium bromide. The reaction was stirred at room temperature for 24 h. With nitrogen bubbling through the solution, the mixture was then refluxed for 2 h. After the mixture was cooled to room temperature, 7 mmol of pyrene-3-carboxaldehyde was added and the solution was further refluxed for 24 h. After the solution was cooled, the solvent was removed under reduced pressure and the residue, in benzene, was chromatographed on an activated alumina column, which gave, after removal of solvent, a yellow solid (54.6% yield), which was purified by the method of Fox et al.[5] immediately prior to polymerization. It was identified by its melting point (mp 87–89 °C).[4]

3. **3-Methylpyrene.** Under an atmosphere of nitrogen 0.997 g of pyrene-3-carboxaldehyde in 26 mL of diethylene glycol was heated to about 80 °C and 1.5 mL of hydrazine was slowly added. Heating was continued, until at 110 °C, about 0.9 g of KOH was cautiously added. The reaction was maintained at 195–210 °C for about 4 h, after which it was allowed to cool to room temperature and poured into ~100 mL of water. The organic component was extracted with Skelly B and passed through an ac-

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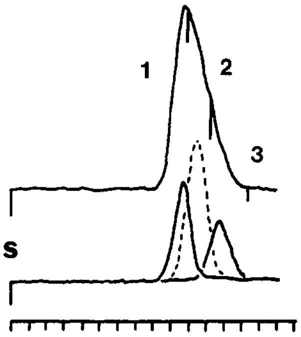

**Figure 1.** GPC elution curve of P2VN-Py. The upper trace is the original polymer, with the three fractions (F1, F2, and F3) indicated. The lower trace is the elution curve of each of these three fractions taken separately. Each tick mark corresponds to 3 mL.

tivated alumina column. The column was washed with 100 mL of 5% benzene in Skelly B. After the solvent was removed by vacuum, the dried material was vacuum sublimed twice, to give 0.491 g of 3-methylpyrene (52.4% yield).

All polymerizations were carried out in benzene using 2,2′-azobis(isobutyronitrile) as initiator (~1 wt %) and heating at 60 °C for 24 h. Polymerizations were carried out in a sealed reaction tube after three freeze-pump-thaw cycles to remove residual oxygen. The resulting polymer was precipitated three times by addition of a benzene solution into rapidly stirred methanol. In the case of P2VN-Py approximately 5 mol % of 3-(bromomethyl)pyrene was added to the reaction mixture as a termination agent, following the work of Holden et al.[2a] The approximate molecular weight (MW) of this polymer was 63 400 (with a polydispersity of 1.71), based on GPC elution and a polystyrene calibration curve (Waters μ-Styragel columns, 500-, $10^3$-, $10^4$-, and $10^5$-Å pore size, $CH_2Cl_2$ mobile phase). We were not able to achieve higher molecular weights than this by reducing the amount of AIBN, while holding the 2-vinylnaphthalene/3-(bromomethyl)pyrene ratio constant. For this polymer we found that there was an apparent low molecular weight component that was not successfully removed by reprecipitation but was removed by GPC using 100 Å + 500 Å μ-Styragel columns with a $CH_2Cl_2$ mobile phase. This component contributed to the fluorescence and prevented an adequate fit of the total fluorescence spectrum (to be discussed below). Since it was not possible in our laboratory to significantly alter the molecular weight of P2VN-Py by chemical methods, we fractionated this polymer using GPC techniques with the 500-, $10^3$-, $10^4$-, $10^5$-Å column set and a $CH_2Cl_2$ mobile phase. This is illustrated in Figure 1.

The mole fraction of pyrene in the polymers was estimated from comparison of the absorption spectra of the polymer and 3-methylpyrene, assuming that (a) P2VN does not absorb above 350 nm and (b) the extinction coefficients for P2VN at 320 nm and 3-methylpyrene are 454 and 31 700[6] L mol$^{-1}$ cm$^{-1}$, respectively. Absorption spectra were taken with a Cary 14 spectrometer.

For the 2-vinylnaphthalene and 3-vinylpyrene copolymer a mixture of the two components was prepared and the polymerization carried out as described in the previous paragraph. The relationship between the mole fraction of 3-vinylpyrene in the reaction mixture and the final purified polymer was excellent (see Table I). While the molecular weight was different for these samples, all spectroscopic observables presented herein correlate simply with $x_{Py}$, the mole fraction of pyrene, in each of the polymers. Unlike P2VN-Py, these polymers did not have a low molecular weight component that was difficult to remove by precipitation techniques. Furthermore, also unlike P2VN-Py, the molecular weight distribution was not strictly mononodal, three of the samples having small but definite shoulders on the GPC trace.[7]

Since one of the objectives of the present study is to characterize singlet energy transfer to pyrene traps, we hoped to obtain one pyrene per chain for the case of P2VN-Py and at least one pyrene per chain for P(2VN-co-3VPy). From our estimated molecular weight and pyrene mole fractions we calculate the average number of pyrenes per chain to be just over 0.5 for P2VN-Py and to range from 0.87 to 6.7 for P(2VN-co-3VPy). If it is true that approximately half the "P2VN-Py" chains are without a terminal pyrene, then our estimation of the quantum efficiency of sensitization (χ; see Results, eq 3) are low by a factor of approximately 2. This could also explain the difference in χ values for P2VN-Py and P(2VN-co-3VPy), to be discussed in section IIIB.

Table I
Polymers Used in This Study

| sample | $x_{Py} \times 10^3$ initial[a] | final[b] | $\bar{n}_{Py}$[c] | $M_w$ | DP[d] | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| | | (i) P2VN-Py | | | | |
| F1 | 50 | 0.90 | 0.58 | 98 600 | 640 | 1.23 |
| F2 | 50 | 1.95 | 0.55 | 43 600 | 283 | 1.16 |
| F3 | 50 | 5.90 | 0.57 | 15 000 | 97 | 1.11 |
| | | (ii) P(2VN-co-3Py) | | | | |
| C1 | 1.2 | 1.9 | 0.87 | 70 800 | 460 | 2.05 |
| C2 | 2.9 | 3.6 | 1.0 | 43 600 | 283 | 1.37 |
| C3 | 6.3 | 8.4 | 3.2 | 58 600 | 381 | 2.21 |
| C4 | 9.6 | 12 | 6.7 | 85 800 | 557 | 2.18 |

[a] Mole fraction of pyrene chromophore in initial polymerization mixture. [b] Mole fraction of pyrene in final polymer. [c] The average number of pyrenes per chain based on the degree of polymerization in column 6 and the pyrene mole fraction in column 3. [d] Based on a GPC calibration curve derived from polystyrene standards and our previous observation that the P2VN molecular weights are approximately twice that of the corresponding elution volume of polystyrene.

**B. Spectroscopic Techniques.** Much of the work to be described involves simple steady-state fluorescence spectra and quenching. These spectra were obtained on a SPEX Fluorolog fluorimeter, with double monochromators for excitation and emission. All solutions had an OD at the excitation wavelength (290 nm, where pyrene has negligible absorption) of <0.1 with a 1-cm path length, so typical concentrations of naphthalene were less than $5 \times 10^{-5}$ mol L$^{-1}$. Those solutions that were outgassed were subjected to freeze-pump-thaw cycles. Because of the long pyrene singlet lifetime, this excited state is particularly subject to oxygen quenching.

For some of the calculations to be presented in the next section an estimate of the absolute quantum yield of fluorescence was required. This was accomplished by comparing the total area under the corrected fluorescence curve of quinine sulfate and 1-naphthol with the species in question in a manner identical with that described by Holden and Guillet.[2a] Our measured values for these quantities in $CH_2Cl_2$ are 0.32 for pyrene bound either at the end or at some site along the polymer chain and 0.058 for the P2VN homopolymer. David et al.[8] have measured $\phi_{fl}^{P2VN}$ in 77 K methyltetrahydrofuran (MTHF) matrices and room-temperature neat films, respectively, obtaining values of 0.13 and 0.04. Transfer efficiencies in films and glasses were determined by assuming that the expression $\phi_{solvent}/\phi_{film} = \tau_{solvent}/\tau_{film}$ holds for the pyrene chromophore.

In order to interpret Stern-Volmer quenching curves in terms of intrinsic rate constants, it is necessary to determine the fluorescence decay rate for the excited species. This was accomplished for either polymer-bound pyrene or 3-methylpyrene at the Center for Fast Kinetics Research at The University of Texas at Austin. In this case excitation of pyrene at 355 nm with a Nd:YAG laser without excitation of the host naphthalene was possible. The resulting pyrene fluorescence decay curve was digitized on a fast transient recorder (Tektronix Model 7912) and fit satisfactorily by a single exponential. The polymer environment did not effect a significant change in pyrene singlet lifetime[9] (see Results). The fluorescence decay rate in degassed dichloromethane solutions for the terminally bound pyrene was the same as that of the copolymer, being about 86 ns in each case.

Studies of $^3Py^*$ quenching were accomplished by monitoring the decay of $^3Py^*$ TT absorption following selective Py excitation (with $N_2$ laser excitation at 337.1 nm) as a function of added quencher (1,4-diphenyl-1,3-butadiene, Eastman Chemical Co.). These decay curves could also be fit to a single exponential at times long compared to the half-width of the laser pulse (~8 ns). These studies were also carried out at the Center for Fast Kinetics

Table II
Quantum Efficiencies of 2-Vinylnaphthalene and Pyrene Copolymers

| | | $\chi$,[a] % | | | | |
|---|---|---|---|---|---|---|
| sample | $x_{Py} \times 10^3$ | $CH_2Cl_2$ | MTHF (77 K) | PS(37k) | PS(200k) | neat film |
| | | (i) P2VN-Py | | | | |
| F1 | 0.90 | 1.5 | 12 | 3.5 | 5.5 | 13 |
| F2 | 1.95 | 2.6 | 18 | 3.0 | 6.0 | 21 |
| F3 | 5.90 | 4.8 | 32 | 3.5 | 6.5 | 35 |
| | | (ii) P(2VN-co-3Py) | | | | |
| C1 | 1.9 | 5.0 | | | | |
| C2 | 3.6 | 9.25 | | | | |
| C3 | 8.4 | 16.25 | | | | |
| C4 | 12 | 23 | | | | |

[a] We estimate that our $\chi$ values have a relative error on the order of ±15%, with a somewhat larger uncertainty for the PS films because of the unknown $\phi_{fl}$ value. The $\phi_{fl}$ values for $CH_2Cl_2$ solution, MTHF glass, and neat films were taken to be 0.058, 0.13, and 0.04, respectively. We have assumed $\phi_{fl}$ for P2VN in PS to be 0.05 (between the solution value and the neat film value).

Research. Diphenylbutadiene, which has a triplet energy of 42 kcal, some 6 kcal below that of pyrene, was recrystallized three times from ethanol. There was very little difference between the triplet–triplet absorption spectrum of 3-methylpyrene and the pyrene chromophore bound to the polymer, whether at the end or at some midpoint site.

**C. Solvent Purification.** Methylene chloride (MCB Reagents) was used without purification, although all polymer solutions were used after being passed through the GPC. No differences in fluorescence lifetimes for the pyrene chromophore were noticed for eluted and noneluted solutions. Ethyl acetate (MCB, spectrophotometry grade) and hexane (MCB Reagents) were fractionally distilled prior to use. Carbon tetrachloride and nitromethane (MCB, both spectroquality) were similarly purified. MTHF (Columbia Organic Chemicals) was refluxed over $LiAlH_4$ and distilled immediately before use, the middle portion being used. Solutions of polymer to be used in this solvent were degassed in quartz tubes, and the tubes were sealed and stored in the dark. Cyclohexane (MCB, spectroquality) was purified by the use of a silica column.

**D. Decomposition of Spectra into Components.** Some of the results to be presented involve the fitting of a spectrum to two or three components (e.g., P2VN monomer, P2VN excimer, and pyrene). A program was written to accomplish this by minimizing the function

$$\delta(a_M,a_D,a_{Py}) = \sum_{i=1}^{N} |S(a_M,a_D,a_{Py};i) - S_{exptl}(i)|^2 \qquad (1)$$

where $S_{exptl}(i)$ is the $i$th point of the experimental spectrum (digitized at regular wavelength intervals) and $S(a_M,a_D,a_{Py};i)$ is a composite spectrum given by

$$S(a_M,a_D,a_{Py};i) = a_M S_M(i) + a_D S_D(i) + a_{Py} S_{Py}(i) \qquad (2)$$

where $S_M(i)$, $S_D(i)$, and $S_{Py}(i)$ are the spectra corresponding to pure P2VN monomer, P2VN excimer, and pyrene (from direct excitation of pyrene in the sample), respectively. Since $S_M(i)$ and $S_D(i)$ overlap strongly in some wavelength regions and cannot be excited independently, they were determined by comparing a P2VN solution spectrum with and without a quencher (e.g., $CCl_4$) present. Since previous work has shown that the M and D fluorescence is quenched at different rates,[3] comparing the quenched and unquenched spectrum of P2VN allows a reasonably accurate determination of these two components. For the case of P2VN films or P2VN in films of polystyrene, the fit used two independent spectra, P2VN alone (M and D combined) and pyrene (from direct excitation), since independent quenching of the M and D species in the film state has not been established.

## III. Results

**A. Energy Transfer in P2VN-Py.** The fluorescence spectra of samples F1, F2, and F3 (in $CH_2Cl_2$) excited at 290 nm (where the direct excitation of pyrene is negligible) show a steadily increasing pyrene component, illustrated in Figure 2. The decomposition into the P2VN-M, P2VN-D, and pyrene components is illustrated for sample F3. In terms of quantum efficiency the spectra of Figure 2 tend to be misleading, since $\phi_{fl}^{Py} > \phi_{fl}^{P2VN}$ (our measured values for these quantities in $CH_2Cl_2$ are $\phi_{fl}^{Py} = 0.32$ for pyrene bound to the polymer chain and $\phi_{fl}^{P2VN} = 0.058$ for the homopolymer). Holden and Guillet[2a] have analyzed their mixed spectra with the relationship

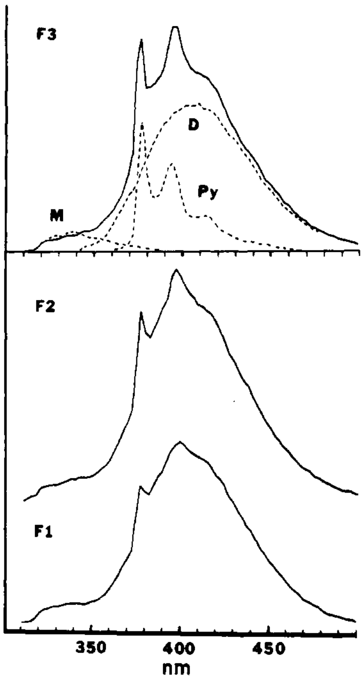

**Figure 2.** Fluorescence spectra of fractions F1, F2, and F3 in $CH_2Cl_2$. The upper trace for F3 illustrates the deconvolution of the spectrum into P2VN-M, P2VN-D, and Py components (all spectra are traces of the digitized spectra).

$$\phi_{fl}^{P2VN} I_{Py} / \phi_{fl}^{Py} I_{P2VN} = \chi/(1 - \chi) \qquad (3)$$

where $\chi$ is the quantum efficiency of energy transfer

$$\chi = \frac{\text{einsteins transferred to pyrene}}{\text{einsteins absorbed by naphthalene}} \qquad (4)$$

Our values of $\chi$, based on the relative areas of P2VN and pyrene ($I_{P2VN}$ and $I_{Py}$, respectively, in eq 3) are in the range 1.5–4.7% for these fractions (see Table II). These values are more than a factor of 2 smaller than those reported by Holden and Guillet[2a] for the corresponding copolymer of 2-naphthylmethyl methacrylate and 9-(bromomethyl)-anthracene (PNMMA-A).[10] It should be emphasized that the experimentally determined $\chi$ values using eq 3 do not depend on any assumption concerning the degree of pyrene

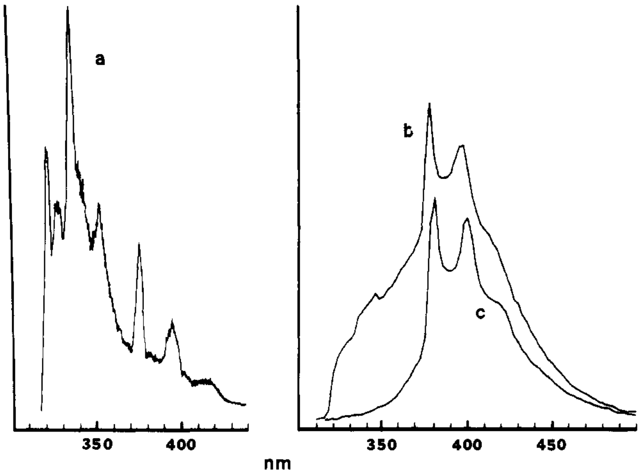

**Figure 3.** Spectra of P2VN-Py (fraction F1) in solid phases: (a) in MTHF glass at 77 K; (b) in polystyrene matrix (MW ~ 37 000) at room temperature; (c) neat film of P2VN-Py at room temperature.

substitution per chain. As discussed in IIA, it is possible that only 50–60% of our chains contain a terminal pyrene group, such that $\chi$ values for polymers containing pyrene chromophores may be larger by a factor of almost 2 than those quoted in Table II. In comparing the P2VN-Py spectra in $CH_2Cl_2$ (a good solvent) with ethyl acetate (a poor solvent), we find that while the appearance of the spectra does change, the $\chi$ values are essentially identical because the quantum yield values are slightly solvent dependent. Likewise addition of a nonsolvent (hexane) to $CH_2Cl_2$ solution up to a point near turbidity does not change the P2VN-Py fluorescence spectrum. We conclude that changes in coil dimensions induced by these solvents must be modest compared to the active radius of naphthalene–pyrene energy transfer. This is not to say that the efficiency of sensitized pyrene fluorescence is independent of the phase containing the P2VN-Py. There are three entries in Table II for solid phases in which dynamic formation of an excimer state is precluded. For a MTHF glass at 77 K the $\chi$ values are approximately an order of magnitude larger than the fluid phase and rival those of Holden and Guillet[2a] for PNMMA-A. In this matrix there is little or no excimer formation (see Figure 3a).[11] In the case of neat films of P2VN-Py the $\chi$ values (at room temperature) are essentially identical with those in 77 K MTHF glasses, despite the strong excimer peak in P2VN films (see Figure 3c). In the case of a film, intercoil energy transfer is obviously possible, and it is also possible that the density of excimer-forming sites is sufficiently high that energy transfer between these sites can occur. One also expects individual polymer coils to be smaller in the film, leading to a large number of naphthalene rings attached to the same chain being within the Förster transfer radius (30 Å for 2-methylnaphthalene–pyrene).[12] The present results do not allow one to distinguish between these various possibilites.

The case of P2VN-Py dissolved in polystyrene (PS) is interesting because Semerak and Frank[13] have shown that the ratio of P2VN monomer and excimer fluorescence ($I_D/I_M$) in PS films is a sensitive function of the molecular weight of the two components. We have estimated the quantum efficiency values for pyrene-sensitized fluorescence in PS films to be between that of fluid solution and neat P2VN-Py films. The concentration of P2VN-Py is reasonably low (<1 wt %) such that the P2VN-Py coils might be expected to be essentially independent of each other. However, Semerak and Frank[13] find that the limiting value of the $I_D/I_M$ for P2VN-Py is achieved abruptly for a weight percent below 0.1%. Thus one may suspect that some local aggregation of the P2VN-Py coils may persist for the spectrum in Figure 3b such that not all energy transfer is intracoil. On the other hand, P2VN compatability with PS is strongly dependent on the molecular weight of the P2VN for a given PS sample.[13] Hence, if aggregation with intercoil energy transfer was the dominant process occurring, one would not expect to see the essentially constant $\chi$ values for the three fractions (see Table II). We also compared PS films in which the PS molecular weight was 37 000 and 200 000, respectively (PS(37k) and PS(200k)). As expected, the fluorescence spectrum of P2VN is changed in these two matrices. In these cases the spectral fit was to a linear combination of the total P2VN fluorescence in the appropriate PS matrix and pyrene (see Figure 3b) (such as was done for neat films of P2VN-Py). While the appearance of the P2VN-Py spectra is dependent on the particular PS matrix, this is primarily because of the underlying P2VN component. The derived $\chi$ values are very similar but there is a tendency for $\chi$ to be slightly larger in the PS(200k) matrix. We interpret this observation as implying a slightly more compact P2VN-Py coil in this matrix, which would enhance the rate of Förster-type energy transfer.

Because our fitting procedure treats P2VN-M and P2VN-D separately for fluid phase spectra, we are in a position to assess the relative quenching of these two species. From consideration of the lack of spectral overlap between the P2VN-D emission and pyrene absorption, it is doubtful that significant Förster energy transfer from P2VN-D to pyrene could occur. Since P2VN-M is the primary precursor[14] of P2VN-D, one would expect the quenching of P2VN-D to follow that of P2VN-M. We have concluded that within the accuracy of our spectral fit procedure this is the case. However, it is probably true that the quenching rate for P2VN-M and P2VN-D would have to differ by a factor of at least 4 before we would pick it up reliably from our fitting procedure because the P2VN *quenching* is actually quite small; the primary spectral feature is the *growth* of the $^1Py^*$ fluorescence (note the ratio of fluorescence quantum yields in eq 3).

**B. Energy Transfer in P(2VN-co-3VPy).** These samples were studied in $CH_2Cl_2$ solution only, for purposes of comparing the derived $\chi$ values (see Table II). The spectra were like those of P2VN-Py except that the pyrene component was increased and the P2VN-M and P2VN-D components were decreased. From Table I we see that the different P(2VN-co-3VPy) samples differed significantly in molecular weights and polydispersities yet a nearly linear correlation of $\chi$ with $x_{Py}$ was observed for these samples. These data are presented in Figure 4, along with the nonlinear correlation for the P2VN-Py samples. As can be seen graphically in Figure 4 the $\chi$ values for P(2VN-co-3VPy) tend to be at least twice that of P2VN-Py of comparable $x_{Py}$. Since for lower $x_{Py}$ values the average number of pyrenes per chain is on the order of unity, the enhancement of $\chi$ may arise in part from a diminution of the average separation of an excited naphthalene chromophore and a pyrene trap (i.e., for the copolymer the pyrene may be located at any point along the coil rather than at the chain ends). However, as pointed out in the Experimental Section, the difference in $\chi$ for these two polymers may also be a result of polymers without a terminal pyrene group in P2VN-Py.

**C. Quenching of the Pyrene Excited State in P2VN-Py and P(2VN-co-3VPy).** The results for the quenching of the $^1Py^*$ or $^3Py^*$ state bound to a P2VN

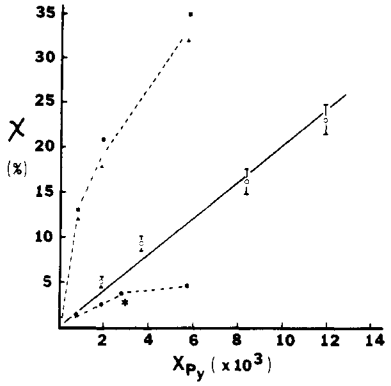

**Figure 4.** $\chi$ as a function of $x_{Py}$ for P2VN-Py in $CH_2Cl_2$ solution (●), P2VN-Py in MTHF glass at 77 K (▲), P2VN-Py in neat film (■), and P(2VN-co-3VPy) in $CH_2Cl_2$ (○). The error bars in this last case are typical for all determinations. The starred point for P2VN-Py ($CH_2Cl_2$) is for the unfractionated polymer.

chain will be discussed together since the observations are very similar for both excited states: (1) For P2VN-Py the pyrene excited state is quenched as essentially as efficiently as the model compound, 3-methylpyrene. (2) For P(2VN-co-3VPy) the pyrene excited state is quenched approximately half as efficiently as 3-methylpyrene.

The simplest interpretation of the first observation is that not only is the terminal pyrene readily accessible to the bulk solution but its diffusion constant (due to segmental motions) must be similar to that of a small molecule. This comment concerning the diffusion constant of the terminal pyrene has to be qualified since we are assuming that the near-neighbor naphthalene groups on the polymer chain do not perturb the pyrene excited state since such a perturbation could enhance quenching rates. However, this "electronic effect", if present, would have to affect $^1Py^*$ and $^3Py^*$ approximately equally, as we will see below.

The second observation is exactly what one would expect for a pyrene molecule that is immobilized. This follows from the classical expression for a diffusion-limited reaction rate constant:

$$k_q = 4\pi(D_Q + D_E)R(N_0/10^3) \quad \text{L mol}^{-1}\,\text{s}^{-1} \tag{5}$$

where $D_Q$ and $D_E$ are the diffusion constants of the quenching molecule and the excited-state molecule, respectively. If the quenching radius ($R$) is unchanged upon attachment of the E molecule to a polymer chain and $D_E^{\text{polymer}} \approx 0$, then

$$k_q^{\text{polymer}}/k_q^{\text{model}} \sim 1/2 \tag{6}$$

is expected.

The singlet quenching rate constants presented in Table III were obtained for $CCl_4$ and $CH_3NO_2$ by fitting the steady-state quenching to the Stern–Volmer expression

$$I_{Py}(0)/I_{Py}(Q) = 1 + K_q[Q] \tag{7}$$

where $K_q = k_q\tau_{Py}$, $k_q$ being the quenching rate constant and $\tau_{Py}$ the lifetime for unquenched excited state. The values of $k_q$ were quite different for $CCl_4$ and $CH_3NO_2$, the latter being typical of a diffusion-limited rate constant.[15] The smaller $k_q$ value of $CCl_4$ is typical of that found for $CCl_4$ quenching of other aromatic singlet states. We found that the molecular weight or mole fraction of pyrene had no effect on the $k_q$ values, within experimental error. Consequently, the values in Table III are averages for the various samples described in Table I. Similarly, there is no significant difference between $k_q$ values in $CH_2Cl_2$ (a "good" solvent) and ethyl acetate (a "bad" solvent) (both solvents have similar viscosities).

Table III
Quenching Rate Constants for $^1Py^*$ and $^3Py^*$

(i) $^1Py^{*a}$

| sample | $k_q \times 10^{-8}$, L mol$^{-1}$ s$^{-1}$ (±10%) CCl$_4$ | $k_q \times 10^{-8}$, L mol$^{-1}$ s$^{-1}$ (±10%) CH$_3$NO$_2$ | $\tau_0$,$^b$ ns (±1%) |
|---|---|---|---|
| P2VN-Py | 1.7 (1.5) | 12 (7.9) | 86 (82) |
| P(2VN-co-3VPy) | | 6.9 (3.5) | 86 (81) |
| 3-methylpyrene | 1.8 (1.5) | 14 (9.2) | |

(ii) $^3Py^{*c}$

| sample | $k_q \times 10^{-9}$, L mol$^{-1}$ s$^{-1}$ (±15%) |
|---|---|
| P(2VN-Py) | 15 |
| P(2VN-co-3VPy) | 8.1 |
| 3-methylpyrene | 16 |

[a] First value for $CH_2Cl_2$ solvent. Value in parentheses is for ethyl acetate as solvent. [b] Pyrene fluorescence lifetimes in degassed solvent. Quenching rate constants were, however, performed in aerated solvent for which the appropriate lifetime was used. [c] Using diphenylbutadiene as quencher and dichloromethane as solvent.

The $^3Py^*$ quenching by diphenylbutadiene was measured by directly determining the change in $^3Py^*$ lifetime as a function of added quencher:

$$k_{^3Py^*} = k^0_{^3Py^*} + k_q[Q] \tag{8}$$

The $^3Py^*$ decay rate was determined by TT absorption ($\lambda_{max} \cong 430$ nm for polymer and model $^3Py^*$) following pyrene excitation at 337.1 nm ($N_2$ laser). The linear relationship expressed in eq 8 was obeyed satisfactorily and the $^3Py^*$ decay could be fit to a single exponential. Once again, different fractions or samples had essentially the same $k_q$ values, with the $k_q$ values for P2VN-Py being larger than those of P(2VN-co-3VPy) by approximately a factor of 2.

## IV. Discussion

**A. Energy Transfer in P2VN-Py and P(2VN-co-3VPy).** Our experiments have paralleled those of Holden and Guillet[2a] in both objective and conclusions. For P2VN copolymers excimer formation is facile and the sensitization quantum efficiency is low. It seems likely to us that the mechanism of sensitization is essentially a single-step Förster process. It is interesting that $\chi$ is relatively larger in the solid phase (films or 77 K glasses). Since extensive excimer formation does occur in films, yet $\chi$ is quite large, we conclude that the following interpretations are consistent with our observations:

(1) Dynamically formed excimers are more effective singlet energy traps than most preformed excimer sites in films or solids. Presumably this arises from the chromophore–chromophore reorientation that is possible, which results in greater stabilization of the excimer state with respect to the "exciton band" (which would be equivalent to the P2VN-M state).

(2) In films (either neat or PS matrices) the density of excimer-forming sites is sufficiently high that energy transfer between these sites is facile, thereby enhancing pyrene sensitization.

These two interpretations emphasize the role of the excimer state as a singlet trap. There is a third possibility for all three solid-state cases, however:

(3) In all solid samples the coil size is small, on the order of $R_0$, the characteristic Förster radius (for 2-methylnaphthalene–pyrene transfer this value is 30 Å).[12] This

certainly seems reasonable in light of the near constancy of $\chi$ for F1–F3 in PS matrices. The higher $\chi$ value in neat films is presumably because both intra- and intercoil energy transfer are operative.[16]

Our data do not distinguish between an interpretation based on the role of the excimer in energy migration ((1) and (2) above), or the effect of coil size ((3) above). If one studied a series of host polymers with a variable terminal trap (thus varying $R_0$), perhaps one could distinguish clearly these possibilites.

We have found that $\chi$ is larger for P(2VN-co-3VPy) than P2VN-Py, even when the mole fraction of pyrene is nearly the same for the two polymers. One reasonable interpretation of this observation is that for P(2VN-co-3VPy) many of the pyrene traps are located nearer the center of mass of the coil such that the probability of an excited naphthalene group residing within $R_0$ is enhanced. All comparisons between P2VN-Py and P(2VN-co-3VPy) are complicated by the uncertainty of the fraction of polymer chains without pyrene traps, especially in the former case. For P2VN-Py our $\chi$ values are obviously a lower limit, by possibly a factor of 2.

We note the possibility for some very interesting theoretical work in deducing the relationship between polymer coil density and trap sensitization for systems of the type described herein.

**B. $^1$Py* and $^3$Py* Quenching in P2VN-Py and P(2VN-co-3VPy).** Quenching of P2VN-Py* and P(2VN-co-3VPy*) was very similar to that of a model small molecule, 3-methylpyrene. As discussed in section IIIB it would appear that the effective diffusion constant of Py* species in P2VN-Py* is similar to that of a small molecule, while for P(2VN-co-3VPy*) this diffusion constant is approximately zero. There is no indication that the Py* species is "protected" by the polymer coil. This latter conclusion is qualitatively like that of Hori et al.,[1] in which triplet benzil was quenched by polystyrene with terminal (PS-A or A-PS-A) or central (PS-A-PS) anthracene groups. However, these same workers did not find any substantial difference between terminal and central anthracenes below degree of polymerization $\sim$500. Also the PS-A or A-PS-A was less efficient than a monomer model molecule (9-methylanthracene) by a factor of $\sim {}^1/_2$ to ${}^1/_3$ for even the lowest degrees of polymerization. It seems likely that the reason for the difference between our results and those of Hori et al.[1] is that we are investigating the kinetics around the polymer coil since our excited species is part of the coil, while their system involves the joint probability that an excited benzil will be in the vicinity of the coil as well as the probability that the triplet benzil will diffuse to the polymer-bound anthracene quencher. It would be very interesting to know what results Hori et al.[1] would have obtained if the quenching of the excited anthracene moiety had been studied, since presumably that system should have many similarities to the one discussed in this article.[17]

It is also interesting to note that in an earlier study in this laboratory[18] of the quenching of the triplet state of P2VN it was found that for the highest molecular weights the piperylene quenching rate constant was ${}^1/_3$ that of 2-ethylnaphthalene, but for lower degrees of polymerization (similar to the samples used in the present study) the quenching rate constants of the monomeric model and the polymer were similar, just as we have found here. It would be quite interesting to prepare P2VN-Py or P(2VN-co-3VPy) of much higher molecular weight to determine if a "steric hindrance effect" is eventually found.

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(6) Sata, K.; Hayashi, N.; Tazuke, S. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 671. We note that McDonald et al.[5] report an extinction coefficient of $\sim$20 000 L mol$^{-1}$ cm$^{-1}$ at 350 nm for poly(vinylpyrene). This would increase our calculated $x_{\mathrm{Py}}$ values if this value is used instead of one for 3-methylpyrene (see text).

(7) In a separate experiment the bimodal fractions were separated on the GPC, but the mole fraction of pyrene and fluorescence spectra of these fractions were the same, despite a significant difference in the molecular weight of the two fractions.

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(9) We note that the fluorescence lifetime and quantum yield of the polymer-attached pyrene is somewhat lower for the corresponding values for pyrene in cyclohexane (450 ns and 0.6, respectively) (Berlman, I. "Handbook of Fluorescence Spectra of Aromatic Molecules"; Academic Press: New York, 1971), although we note that a lifetime of only about 60 ns has been obtained for directly excited pyrene existing as a guest in a naphthalene crystal (Powell, R. C. *J. Chem. Phys.* **1973**, *58*, 920).

(10) In ref 2a sample 2, PNMMA-A, had $M_n$ = 41 000 (DP $\simeq$ 182) and $x_{\mathrm{Py}}$ = 0.005, which is similar to the average for our samples F2 and F3, for which $\chi$ is 2.6–4.8% (cf. for PNMMA-A $\chi$ = 10–13% for THF and toluene, respectively).

(11) In fact, there is a broadening to the red in this spectrum that is not observed for 2-ethylnaphthalene, so there may be a small residual excimer component.

(12) Berlman, I. "Energy Transfer Parameters of Aromatic Compounds"; Academic Press: New York, 1973.

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(14) But, as we have argued in earlier work, P2VN-M is not necessarily the sole precursor state of P2VN-D.[3]

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(16) We note that in ref 2a for PNMMA-A the $\chi$ value for neat films was unity.

(17) We note that in a study of polystyrene with either pendent or backbone diphenylanthracene (DPA) the quenching rate constant of polymer-bound $^1$DPA* by *N,N*-dimethyl-*p*-toluidine was approximately half that of free DPA. For $CCl_4$ quenching there was little or no difference between polymer-bound and free DPA (Bentz, J. P.; Beyl, J. P.; Beinert, G.; Weill, G. *Eur. Polym. J.* **1975**, *11*, 711.

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