aqueous solution of SP2VN at pH 6 did not absorb any perylene, although some evidence of trapping was obtained in subsequent experiments using higher concentrations of perylene. The concentration of perylene was estimated to be 1.4×10^{-6} M by UV absorption measurements. No perylene was found dissolved in water treated with ether solutions of perylene in control experiments. When SP2VN was dissolved in THF–methanol along with 1.5×10^{-6} M perylene, no perylene emission was observed when the naphthalene groups in the polymer were excited at 310 nm, although direct excitation of the perylene at 330 nm showed the expected emission. Thus, we conclude that only in the dilute NaOH solution is the perylene trapped in proximity to the naphthalene groups so that efficient energy transfer can occur. In organic solution at these concentrations the traps are apparently uniformly dispersed in solution rather than concentrated in the pseudomicellar structure of the polymer.

In conclusion, it appears possible to design aromatic polyelectrolytes from polymers containing both hydrophobic and hydrophyllic groups, which under appropriate conditions of pH and ionic strength will hypercoil to form pseudomicellar conformations in aqueous solution. These conformations will reversibly trap hydrophobic organic molecules in the interior of the polymer coil. If these molecules have the correct photophysical characteristics, as in the case of naphthalene and perylene, the trap can be selectively excited by light absorbed only by the naphthalene groups. Presumably the excitation reaches the trap via singlet energy migration and transfer. This represents a novel application of the antenna effect in synthetic polymers.

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Registry No. Perylene, 198-55-0.

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Fluorescence and Energy Migration in 4-Vinylbiphenyl Homopolymer and Alternating and Random Copolymers of 4-Vinylbiphenyl with Methyl Methacrylate

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ABSTRACT: The fluorescence properties of random and alternating copolymers of 4-vinylbiphenyl and methyl methacrylate are compared with those of a model polymer with ca. 1 mol % 4-vinylbiphenyl (remainder methyl methacrylate) and the homopolymer of 4-vinylbiphenyl. For the alternating copolymer there is no excimer fluorescence, unlike the random copolymer. The singlet energy migration constant (Λ_S) was estimated by the method of comparative fluorescence quenching. It was found that Λ_S is larger for the alternating copolymer than for the random copolymer (ca. 1.1×10^{-5} and 3×10^{-7} cm^2/s, respectively). Λ_S is estimated to be 0 for the homopolymer. These values are smaller than values for the corresponding naphthalene copolymers.

Introduction

It is well-known that energy migration along polymer chains can be terminated via excimer formation. Introducing bulky groups[1] on the chromophore is an effective way to reduce excimer formation; however, the energy transfer rate may also be reduced. Fox and co-workers noted in their early polymer photophysical experiments that alternating naphthalenic polymers exhibited little or no excimer fluorescence.[2] Our previous studies on alternating copolymers of 2-vinylnaphthalene with methyl methacrylate and methacrylic acid demonstrated not only that excimer formation was essentially eliminated but also that energy transfer rate was still significant.[3] This report is an extension of this previous study. The nonplanar molecule[4,5] biphenyl was selected to make an alternating copolymer. The Förster self-transfer distance is very small for this chromophore, ca. 3.11 Å.[6]

Singlet energy migration rates were estimated for the homopolymer and the alternating and random copolymers by the method of comparative quenching.[8] In contrast to the interpretation of Abuin et al.[7] no singlet energy migration was observed in the homopolymer, and the average energy migration distance (L_S) for the alternating copolymers was larger than that of the random copolymers, similar to the results of our previous study.[3] We will return to this point in the Discussion.

Experimental Section

A. Materials and Polymerization. The starting materials for sample preparation were 4-vinylbiphenyl (4VBP) (COC), ethylaluminum sesquichloride ($Et_2AlCl \cdot EtAlCl_2$) (Aldrich), and methyl methacrylate (MMA) (J. T. Baker). 4VBP was purified[9] by chromatographic adsorption on alumina from a 2:1 (v/v) benzene–*n*-hexane solution and recrystallized from methanol, mp

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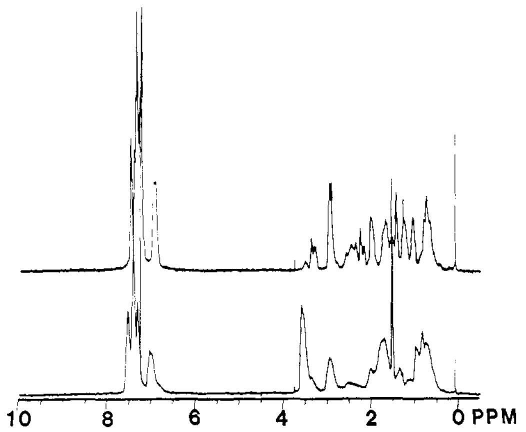

Figure 1. 500-MHz ^1H NMR of alternating (top) and random (bottom) copolymers of 4-vinylbiphenyl and methyl methacrylate at 45 °C in $CDCl_3$. The sharp superimposed peaks are solvent peaks.

Table I
Mole Percent of VBP in Polymer

polymer type	mol % of VBP NMR	mol % of VBP UV[a]
alt	47.9	56
random	35.4	42
model		~1
homo		100

[a] Biphenyl extinction coefficient taken to be 17 200 cm^2 mol^{-1}.[11]

115 °C. Purification of solvents and other materials and the conditions of copolymerization have been described previously.[3]

B. Characterization of Polymer and Fluorescence Measurement. A Waters HPLC and four μStyragel columns (10^2-, 10^3-, 10^4-, and 10^5-Å pore size) were used to determine molecular weight of all polymers using monodisperse polystyrene samples as standards. We note that alternating copolymer tends to have higher molecular weight than random copolymer or homopolymer.

The ^1H NMR spectra of P(4VBP-*alt*-MMA) and P(4VBP-*co*-MMA) were obtained at 500 MHz on a GE spectrometer (Figure 1). As expected, the spectrum of the alternating copolymer is much more resolved than that of the random copolymer due to its regularity of chromophores. The copolymer compositions obtained from UV absorption spectra and H -NMR, however, were not consistent with each other (see Table I). We speculate that the biphenyl extinction coefficient is slightly perturbed in the polymer.

All steady-state fluorescence spectra and lifetime measurements were carried out in N_2-purged THF solutions that were approximately 10^{-6} M in biphenyl groups. An excitation wavelength of 266 nm was used (OD = 0.1). A Spex Fluorolog 2 with a 450-W xenon lamp and an R508 photomultiplier were used. The steady-state fluorescence quenching was determined from both the intensity of biphenyl emission at 320 nm and the integration of intensity between 290 and 320 nm. These results were consistent with each other.

Lifetime measurements were carried out at The Center for Fast Kinetic Research, University of Texas at Austin. A Q-switched Nd:YAG laser (λ = 266 nm, 32 mJ, 200-ps pulse width) was used as the excitation source. The laser beam is circular (8-10-nm diameter) and the intensity profile is approximately Gaussian. Signal-averaging routines were used to improve the signal-to-noise ratio of the collected data. Pulse-to-pulse reproducibility is usually better than 10%. A Tektronix R7912 recorder was used for emission measurements. All decay data were fit to single- or double-exponential decay functions. Different time ranges were employed to check the consistency of the fits.

Results and Discussion

A. Fluorescence Spectroscopy. The spectra of alternating and model copolymers are composed of a structureless emission peak with the maximum at 320 nm[10] (Figure 2), but the excimer emission, which centered at about 395 nm, was the dominant feature in the homopolymer (Figure 2). For the random copolymer, both monomer and excimer emissions were observed, with the intensity of the excimer about 45% that of the monomer emission (Figure 2). The emission spectra do not change upon quencher addition for alternating and model copolymers. However, excimer emission is diminished much more than monomer emission for homopolymer and random copolymer. This is typical of other excimer-forming polymers.[3,8] We note that it is possible to totally quench the excimer component for the random copolymer, but this is not the case for the homopolymer.

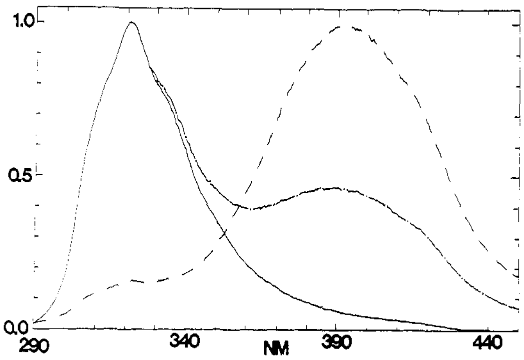

Figure 2. Comparison of fluorescence spectra of the alternating (—) and random (- • -) copolymers of 4-vinylbiphenyl and methyl methacrylate and the homopolymer P4VBP (- - -). The model polymer spectrum is essentially identical with that of the alternating copolymer. Solvent, THF; excitation wavelength, 266 nm.

Table II
Fluorescence Decay Fitting Parameters for P(4VBP-MMA)[a]

	320 nm[b]	400 nm[b]
model (~1% VBP)	11.9 ns	
alt (~48% VBP)	8.7 ns	
random (~36% VBP)	14.5 ns (~37%), 5.3 ns (~63%) ($\langle\tau\rangle$ = 9.7 ns)[c]	18.5 ns (~51%), 5.4 ns[d] (~-49%) ($\langle\tau\rangle$ = 23.6 ns)[c]
homo (100% VBP)	13.1 ns (~7%), 1.7 ns (~93%) ($\langle\tau\rangle$ = 6.0 ns)[c]	26.4 ns (~70%), 12.4 ns (~30%) ($\langle\tau\rangle$ = 24 ns)[c]

[a] Room-temperature THF solution, 10^{-6} M in biphenyl, N_2 purged, excited at 266 nm. [b] For the biexponential decays, the preexponential factors are given as a percent calculated as $(A_i/(A_1 + A_2)) \times 100$. [c] $\langle\tau\rangle = \sum A_i\tau_i^2/\sum A_i\tau_i$, eq 3. [d] Rise time, i.e., A_i for this component, is negative and almost equal to the preexponential component. In this case the percent given is based on the absolute values of the A_i's (*b*) but $\langle\tau\rangle$ is computed with the appropriate signs for the A_i's.

Only a single exponential was required to fit the decay curves for the alternating and model copolymers, even with the addition of CCl_4. As we have argued previously,[3] this is expected if there is significant singlet migration since the emitting state experiences an averaged environment during its lifetime. The lifetime we obtain for the model polymer (ca. 11.9 ns) is similar to the value of 4-isopropylbiphenyl (ca. 13.7 ns in cyclohexane[11]). See Table II for preexponential factors and lifetimes.

Analysis of fluorescence decays for P4VBP and P(4VBP-*co*-MMA) required a dual-exponential decay function for emission monitored at 320 or 400 nm; i.e.[12]

$$I(t) = A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$$

A negative preexponential coefficient in the fitting function of the P(4VPB-*co*-MMA) 400-nm emission implies that

Table III
Compilation of Rate Constants and Energy Migration Constant

	K_{SV},[a] M^{-1}	$\tau_0 \times 10^{-9}$, s $\lambda^{em} = 320$ nm	$k_q = K_{SV}/\tau_0$ $(M^{-1}\,s^{-1}) \times 10^9$	Λ_S/D_Q[b]	L_S,[c] Å	MW
model	82.0	11.9	6.9	0	0	2×10^4
alt	105	8.7	12	0.75	31	5×10^5
homo	38.2	$\langle\tau\rangle = 6.0$	6.4	<0	0	2×10^4
random	76.9	$\langle\tau\rangle = 10.9$	7.0	0.02	8	4.7×10^4

[a] For CCl_4 quenching (see text). [b] From eq 5 of text. [c] From eq 6 of text.

excimer formation occurs via a mechanism analogous to the classical Birks scheme, i.e., $^1M^* + M \rightarrow {}^1D^*$, or via exciton migration to an excimer-forming site.[13] However, no negative preexponential coefficient was obtained in the excimer decay function of P4VBP, which suggests the existence of a high density of preformed excimer sites such that excimer formation is too rapid to be resolved by our experimental system.

B. Fluorescence Quenching and Singlet Energy Migration in the THF Solution. Following our previous work,[3] singlet energy migration rates are estimated via a comparative quenching study. In this method, CCl_4 was used as a quencher and the steady-state Stern–Volmer quenching constants, K_{SV}, were obtained by a least-squares fit to a straight line; i.e.

$$I_0/I_Q = 1 + K_{SV}[Q] = 1 + k_q\tau_E[Q] \qquad (1)$$

where τ_E is the excited-state lifetime and k_q is the second-order quenching constant. We note that our value of K_{SV} for the model polymer is very similar to that reported by Abuin et al.[7] for an analogous biphenyl loading. However, our K_{SV} value for the random copolymer is ca. 1.7 times higher than that for their corresponding polymer. We speculate that this is the result of a longer singlet lifetime for our samples. This could result from the extent of solvent degassing, purification, etc. It is straightforward to derive k_q from eq 1 for model and alternating polymers due to their single-exponential fluorescence decay, which yields τ_E. Since biexponential decay functions are required for P4VBP and P(4VBP-*co*-MMA), it is assumed that each component is independently quenched by CCl_4 with the same k_q value from which τ_E was taken to be a weighted average of its components.[13] Thus eq 1 can be written as

$$I_0/I_Q = 1 + k_q\langle\tau\rangle[Q] \qquad (2)$$

where

$$\langle\tau\rangle = \sum_i A_i\tau_i^2 / \sum_i A_i\tau_i \qquad (3)$$

In order to interpret k_q, the modified Smoluchowski–Einstein equation was used:[14]

$$k_q = 4\pi N_0(D_B + D_Q + \Lambda_S)PR \times 10^{-3} \qquad (4)$$

where D_B and D_Q are the diffusion constants of the excited biphenyl and quencher, respectively. Λ_S is the singlet energy migration rate. P represents the quenching probability per collision, R is the sum of radii for B and Q, and N_0 is Avogadro's number. We assume that the value of PR is the same for all polymers studied. For any chromophore attached on the polymer chain, it can be assumed that $D_B = 0$ and $\Lambda_S = 0$ for the model polymer. From eq 3 one obtains

$$\Lambda_S/D_Q = (k_q^{\text{poly}} - k_q^{\text{model}})/k_q^{\text{model}} \qquad (5)$$

On the basis of the one-dimensional random walk, the excitation diffusion length L_S can be evaluated from the equation

$$L_S = (2\Lambda_S\tau_E)^{1/2} \qquad (6)$$

Results are shown in Table III. The value of D_{CCl_4} used in the calculation was 1.5×10^{-5} cm^2/s.[15]

Our conclusion that $\Lambda_S = 0$ for the homopolymer is at first glance in contradiction to the discussion of Abuin et al.,[7] who invoke the role of energy migration in the observed excimer/monomer fluorescence ratio. However, it should be emphasized that the value of Λ_S obtained from the comparative quenching method is really an effective migration constant that is an ensemble average over monomeric excited states. Some of these are very rapidly trapped (and hence inefficiently quenched) while others happen to be formed in a sequence for which trapping at an excimer-forming site is less likely, and hence the quenching is more efficient. Thus our conclusion that $\Lambda_S = 0$ for the homopolymer does not mean that energy migration does not enhance excimer formation but rather that the average number of energy hops in the homopolymer is small.

However, there is one point of disagreement between the interpretation of Abuin et al.[7] of their results and our point of view. They find that the quantum yield of monomer fluorescence is linearly proportional to K_{SV}, which in turn they take to imply that the ratio k_{MF}/k_q (monomer radiative rate divided by quenching rate) is constant for all copolymer compositions. Our results are interpreted based on the idea that k_q is dependent on composition through Λ_S and eq 4. Our values of $\langle\tau\rangle$ should be proportional to the fluorescence quantum yield if k_{MF} is constant except for the following complication: any fluorescence component that decays too rapidly to be followed by our single photon detection system will not contribute to $\langle\tau\rangle$, and hence these values overestimate the monomer fluorescence quantum yield. (This is an argument similar to so-called "static quenching".)

Conclusions

The present paper can be regarded as an extension of our earlier work on alternating 2-vinylnaphthalene–methyl methacrylate or methacrylic acid copolymers.[3] The basic observations are as follows:

(1) Excimer fluorescence is essentially absent in the alternating copolymer, unlike the random copolymer.

(2) The singlet energy migration constant (Λ_S) is larger for the alternating copolymer than for the random copolymer. There seems to be little or no energy migration in the homopolymer P4VBP (see Table III).

It is interesting that the measured value of Λ_s is lower for P(4VBP-*alt*-MMA) than the corresponding naphthalenic copolymer.[3] This is reasonable based on the lower Förster radius for self-transfer for 4-methylbiphenyl relative to 2-methylnaphthalene (6.41 vs. 11.02 Å, respectively[7]). This is consistent with our earlier studies of singlet–singlet annihilation in the homopolymers P2VN and P4VBP.[16] The difference between the random and alternating copolymers is more extreme in the present system, although it should be pointed out that the method of comparative quenching becomes less accurate as Λ_S/D_Q approaches zero.

Our main objective in the present paper is the elucidation of the photophysical properties of the alternating copolymer of methyl methacrylate and 4-vinylbiphenyl rather than a further exploration of random copolymer systems. We conclude that alternating polymer systems represent an interesting class of copolymers that permit facile down-chain energy transfer, partially as a result of diminished excimer formation rates.

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Registry No. P(4VBP-*alt*-MMA) (copolymer), 82530-42-5; P4VBP (homopolymer), 25232-08-0; CCl_4, 56-23-5.

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Fluorescence of Vinyl Aromatic Polyelectrolytes: Effects of Conformation, Concentration, and Molecular Weight of Sodium Poly(styrenesulfonate)

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ABSTRACT: Conformational behavior of atactic sodium poly(styrenesulfonate) has been investigated by the use of fluorescence spectroscopy. Measurement of the excimer to monomer fluorescence intensity ratio, $I_{\rm E}/I_{\rm M}$, provides information relating to specific conformational populations in vinyl aromatic polymers. The overall size of the polyelectrolyte coils was varied extensively through control of ionic strength of the solvent, and the influence of the overall conformation of the polyelectrolyte on $I_{\rm E}/I_{\rm M}$ was monitored. As the shape of the chain changes from a highly extended, rodlike form to a loose coil, $I_{\rm E}/I_{\rm M}$ was found to be approximately constant, implying that local bond conformations are almost invariant. Increased molecular weight was found to increase $I_{\rm E}/I_{\rm M}$ in a manner that cannot be explained solely on the basis of end effects. The concentration dependence of $I_{\rm E}/I_{\rm M}$ was similar to that observed in polystyrene: no effect is seen for $0.01 \le c \le 2$ g/L, and above 2 g/L $I_{\rm E}/I_{\rm M}$ increases only very gradually. Absorbance spectra were recorded and found to exhibit slight sensitivity to conformational changes.

Introduction

Fluorescence behavior of neutral polymers, containing either naturally present chromophores or fluorescent probes, has been studied in detail by a number of research groups.[2-30] One reason for this interest, particularly for vinyl aromatic polymers, is that fluorescence emission is sensitive to specific local conformations and configurations of the polymer chain. For example, Hirayama[31] demonstrated with low molecular weight analogues of phenyl-containing polymers, such as polystyrene, that intramolecular excimer formation occurs only when the number of carbon atoms separating phenyl rings is equal to three (the "$n = 3$" rule). Later, Bokobza, Jasse, and Monnerie[32] investigated the fluorescence of three polystyrene model compounds (2,4-diphenylpentane, 2,4,6-triphenylheptane, and 2,4,6,8-tetraphenylnonane) and found that isotactic configurations were more favorable for excimer formation than were syndiotactic configurations: the ratio of excimer to monomer fluorescence intensity, $I_{\rm E}/I_{\rm M}$, was up to 20 times higher for the isotactic model compounds than for the syndiotactic compounds. These results have been corroborated in polymeric systems by Longworth[3] and Ishii et al.[4] In the case of isotactic (or meso) diads, excimer formation is associated with the trans–trans conformation. Thus, by measuring $I_{\rm E}/I_{\rm M}$ in vinyl aromatic polymers, such as polystyrene, one may probe local conformational behavior, specifically, the presence of trans–trans conformations in isotactic diads along the chain. Excimer fluorescence may occur from trans–trans conformations formed either prior to excitation or by a conformational transformation after excitation. Therefore, we may take advantage of the sensitivity of fluorescence spectroscopy to monitor local polymer behavior. In this paper, we report on local orientations of a polyelectrolyte chain and how these orientations change as the macroscopic dimensions of the coil vary.

There have recently been a number of investigations of fluorescence and absorbance phenomena in aqueous po-

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