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Photophysics of Block Copolymers of 2-Vinylnaphthalene and Vinyldiphenylanthracene: Unidirectional Energy Transfer

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ABSTRACT: Block copolymers of 2-vinylnaphthalene and vinyldiphenylanthracene (VDPA) were prepared by using anionic polymerization techniques. Sensitization of the DPA singlet state by that of the naphthalene moiety is very efficient in THF solutions (ca. 0.75–1.00). The quantum efficiency of sensitization as measured by steady-state fluorescence spectroscopy is higher than that based on lifetime shortening. This implies that some sensitization occurs very quickly (e.g., "contacts" between donor and acceptor) or that a nonemitting precursor state of the observed naphthalene singlet can sensitize the DPA. By virtue of the block nature of this copolymer energy migration is "unidirectional" (i.e., from one block to another). In principle, this approach could be extended to a series of chromophores.

Introduction

In recent years there has been a rapid growth in the field of polymer photophysics both from the point of view of using spectroscopic tools to elucidate polymer conformation and morphology and for the purpose of designing polymers that have interesting photophysical characteristics.[1] The present report is in the latter catagory. Using anionic polymerization techniques, we have prepared block copolymers of 2-vinylnaphthalene (2VN) and vinyldiphenylanthracene (VDPA; systematic name: 9-(*p*-ethenylphenyl)-10-phenylanthracene).

We had several motivations for pursuing this synthesis: (1) A great deal of photophysical work has been carried out on P2VN[2] but always on free-radical polymerized samples. Does the method of synthesis modify the photophysics? (2) An earlier report stated that vinyldiphenylanthracene did not anionically polymerize with a cumyl potassium initiator.[3] We hoped conditions could be found that would allow this interesting polymerizable chromophore to be block polymerized. (3) Block copolymers of the type P2VN-*b*-VDPA would be expected to exhibit "unidirectional energy transfer" in the sense that excited states created in the naphthalene block will inevitably be directed toward the VDPA block. (Of course truly spatially directed energy transfer would require that the polymers themselves have a sense of direction such as would be the case if one end is covalently bound to a substrate.) Block copolymers of the present type represent an interesting new class of "proton-harvesting polymers" that are limited only by the availability of polymerizable chromophores.

Experimental Section

Monomer Purification. 2-Vinylnaphthalene (Aldrich) was sublimed twice and then collected in an ampule into which benzene was distilled. Vinyldiphenylanthracene was prepared as previously described,[4] further purified on an alumina column with benzene as eluent, and then precipitated with methanol. After drying under high vacuum, the material was placed in an ampule and again evacuated, and benzene distilled in. The solution was frozen and lyophilized, then pumped for 12 h at 10^{-6} Torr. Fresh benzene was distilled in, and the ampule sealed and removed from the line. This ampule was sealed to another apparatus which was evacuated, filled with argon, and placed in a glovebox. Sodium metal, freshly cut and with bright surfaces, was added to the apparatus, which was then removed from the box and replaced on the vacuum line, evacuated to 10^{-6} Torr, and sealed off. The sodium was distilled into the main chamber to form a mirror, and the very pale yellow benzene solution of VDPA was added via a break seal. The solution immediately turned bright blue, indicating formation of the dianion. It was then filtered through a fine-porosity fritted disk and collected in ampules.

Table I
Degree of Polymerization and Composition Data

polymer	$\overline{\mathrm{DP}}$	$\overline{\mathrm{DP}}_{\mathrm{naph}}$	$\overline{\mathrm{DP}}_{\mathrm{DPA}}$
P2VN-*b*-VDPA-a	125[a]	120[b]	5[b]
P2VN-*b*-VDPA-b	210[a]	25	185
P2VN-*b*		25[a]	

[a] Estimated from GPC, taking the degree of polymerization to be equal to PS standards (see text). [b] Estimated from absorption spectroscopy.

Initiator Preparation and Polymerization. *n*-Butyllithium initiator was prepared in hexane from lithium dispersion, and *n*-butyl bromide under high vacuum conditions as described by Morton and Fetters.[5] Solvent purification and polymerizations also followed their general methods; however, we found it advantageous to break the initiator ampule while the reactor was still on the vacuum line so that the hexane could be pumped off and replaced with benzene to avoid problems with precipitation of the growing polymer chains. The 2VN monomer was added after sealing from the line, and over a period of 10 min the solution attained the dark red color of the living polymer. In one case the VDPA solution was added directly (P2VN-*b*-VDPA-a). In the second case an ampule of living P2VN was sealed off, and the remainder terminated with thoroughly degassed alcohol (P2VN-b). The ampule was then sealed to another apparatus along with the VDPA ampule, and the second block was added to the living polymer (P2VN-*b*-VDPA-b). Unfortunately this latter sample had such a high content of VDPA that it was not very interesting photophysically.

The degree of polymerization of the polymer samples was determined on a Waters GPC apparatus (500-, 10^3-, 10^4-, 10^5-Å u-Styragel columns) with THF mobile phase and polystyrene MW standards. An example of a gel permeation chromatography (GPC) elution curve for P2VN-*b*-VDP-a (and the fractions discussed in more detail below) is given in Figure 1. Our estimated degree of polymerization for these polymers is given in Table I.[6]

Photophysics. Absorbance and steady-state fluorescence measurements on the eluent solutions were carried out on a Hewlett-Packard Model 8451A spectrophotometer and a Spex Fluorolog 2 fluorimeter. All fluorescence spectra are uncorrected for photomultiplier response and were taken with aerated solutions. Excitation spectra were corrected for variation of the intensity of the excitation source with wavelength. Fluorescence decay was measured by using a synch-pumped, cavity dumped dye laser (doubled to 290 nm) pumped by a Nd:YAG mode-locked laser. This system has an overall instrumental response function width of ca. 400 ps. The fluorescence decay was analyzed by reconvolution of a multiple-exponential decay function with the instrument response function.[7] In most cases a simultaneous fit of data for two different time scales was carried out when widely different lifetimes were present (see Results). For three exponential fits of fluorescence decay over a single time period, χ^2 values on the order of 1–2 were obtained. For simultaneous fits to two time scales, the χ^2 value was significantly worse (<2), but the values of the fitting parameters were only slightly changed. To present a compact representation of the time-dependent data

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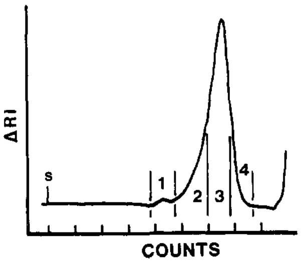

Figure 1. GPC trace for P2VN-*b*-VDPA-a and samples discussed in text. Detection by differential refractive index; injection indicated by S.

we present the results of the "global" fit. It is very likely the case that a three-exponential function is not a physically realistic fitting function but is adequate to compute the average lifetime (eq 2) required for χ_t calculation (eq 3). A more detailed study of the time dependence of this system and other polymers with simultaneous down-chain energy transfer and trapping will be the subject of later publications.

Results

Steady-State Photophysics: Absorption, Excitation Spectra, Fluorescence, and Quantum Efficiency of Sensitization. The absorption spectra of the homo-P2VN or P2VN-*blk*-VDPA block polymers were the expected superposition of 2-naphthyl and DPA components. The ratio of naphthalene to DPA moiety was estimated from the optical density (OD) at 320 and 376 nm (ϵ_{naph} (320 nm) = 454 M^{-1} cm^{-1}, ϵ_{DPA} (376 nm) = 14000 M^{-1} cm^{-1}) and is the basis for the estimated degree of polymerization (DP) for the individual components of the block polymers given in Table I.

The excitation spectra were also a superposition of the naphthyl and DPA components, and by comparing the absorption and excitation spectrum of the DPA component (λ_{obsd} = 440 nm), one can estimate χ_{ss}, the quantum efficiency of sensitization of DPA per naphthyl excited state created.[8] Simply stated, if the excitation spectrum of the acceptor fluorescence is identical with the absorption spectrum, then χ_{ss} is unity, while if only the acceptor appears in the excitation spectrum, then χ_{ss} is zero.

If there exists a wavelength at which only the donor absorbs (λ_D), then one may write

$$\chi_{ss} = \frac{I_A(\lambda_D)}{I_A(\lambda_A)}\,\frac{f_A(\lambda_A)}{f_D(\lambda_D)} \cong \frac{I_A(\lambda_D)}{I_A(\lambda_A)}\,\frac{\mathrm{OD}_A(\lambda_A)}{\mathrm{OD}_D(\lambda_D)} \qquad (1)$$

where the second form is appropriate for low-OD solutions. In eq 1 $I_A(\lambda)$ is the intensity of the acceptor component in the excitation spectrum at excitation wavelength λ, and λ_A and λ_D correspond to wavelengths absorbed exclusively by the acceptor and donor, respectively, while $f(\lambda)$ and $\mathrm{OD}(\lambda)$ refer to fraction of light absorbed and optical density. The equations become more complex if the donor and acceptor overlap strongly for all wavelengths for which the donor absorbs. There always exists a set of λ_A since the acceptor has a lower energy onset of absorption than the donor. The only other assumption in eq 1 is that the fluorescence quantum yield of the acceptor is the same regardless of whether it is directly excited or sensitized (all methods make this assumption). This might not be the case if the local environment of acceptors that are efficiently sensitized is quite different from the average acceptor environment and the fluorescence quantum yield is environmentally sensitive. In the present case this would be quite surprising since both the polymer and the solvent are hydrocarbons. For the block copolymers χ_{ss} is very high. For P2VN-*b*-VDPA-a different molecular weight fractions were collected (see the Experimental Section and Figure 1), and χ_{ss} was determined for these separately. The naphthalene/DPA ratio was not constant over this collection of samples, as determined by absorption spectroscopy. These results are in Table II. For P2VN-*b*-VDPA-b the fluorescence yield of the naphthyl moiety is essentially zero (i.e., $\chi_{ss} \cong 1$) and the DPA fluorescence spectrum in this polymer is noticeably red-shifted relative to P2VN-*b*-VDPA-a (Figure 2). We presume this is the result of emission from partially trapped singlet states. While PVDPA does not exhibit classical excimer fluorescence, some sort of "weakly bound excimer state" does seem to exist.

Table II
Composition and χ Values for Samples of P2VN-*b*-VDPA-a (THF Solvent)

sample	naphthalene/DPA[a]	$\bar{\mathrm{D}}\mathrm{P}$[b]	χ_{ss}	χ_t[c]
1	8.6	630	0.64	0.72 (0.81)
2	13.5	240	1.00	0.69 (0.79)
3	23.8	110	0.86	0.57 (0.67)
4	25.2	55	0.76	0.46 (0.59)

[a] From absorption spectroscopy. [b] Based on $\bar{\mathrm{D}}\mathrm{P}$ of polystyrene standards. [c] Based on eq 3 with P2VN-*b* as a model compound. Values in parentheses are calculated by using a biexponential fit to P2VN-*b*-VDPA-a decay data.

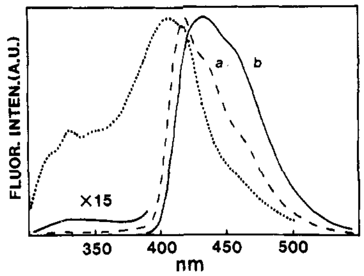

Figure 2. Fluorescence spectra of P2VN-b (···), P2VN-*b*-VDPA-a (---) and P2VN-*b*-VDPA-b (—). All were in THF, N_2 bubbled, and excited at 290 nm. Note the scale change for the DPA portion for P2VN-*b*-VDPA-b.

The anionically polymerized P2VN-b exhibits a clear excimer fluorescence, and both the monomer and excimer are blue-shifted relative to free-radical polymerized P2VN[9] (approximately 10 and 5 nm, respectively). We speculate that this is the result of a different tacticity for the anionically polymerized material. Also the excimer/monomer ratio is smaller than previously reported free-radical P2VN,[9] but this could be a molecular weight effect.[10] It is clear that in P2VN-*b*-VDPA-a the naphthalene excimer is suppressed relative to P2VN-b (Figure 2). This is expected if energy transfer competes successfully with excimer formation for the precursor monomeric excited state.

The variation in χ_{ss} for the different GPC fractions of P2VN-*b*-VDPA-a presented in Table II is interesting. Samples 1–4 roughly represent a systematic decrease in the length of the DPA segment, and for samples 2–4 χ_{ss} decreases (although all values are quite high). Sample 1 has an anomalously low χ_{ss} value in this series, and stands away from the main GPC peak (see Figure 1). On the basis of the time-dependent results (next subsection) we believe this sample is a mixture of P2VN-*b*-VDPA and homo-PVDPA.[11] Since the latter component cannot be sensitized by naphthalene, the average χ_{ss} is decreased, even though the naphthalene lifetime is the shortest for this sample. We note that characterizing a polymer by molecular weight (elution volume), absorption spectrum, and fluorescence sensitization is one interesting method to characterize a copolymer via GPC.

Time Dependence of Sensitized Fluorescence. Excitation at 290 nm is absorbed primarily by the naphtha-

Table III
Multiexponential Fitting Functions for Fluorescence Decay[a]

	naphthalene (340 nm)			DPA (450 nm)		
sample	τ_1/a_1	τ_2/a_2	τ_3/a_3	τ_1/a_1	τ_2/a_2	τ_3/a_3
P2VN	1.86/0.423[b]	5.43/0.577[b] $\bar{\tau}$ = 3.92[c]				
P2VN-*b*-VDPA-a						
1	0.45/0.931	5.42/0.056 $\bar{\tau}$ = 1.11[c]	29.9/0.013	0.26/−0.850	6.18/1.000	29.8/0.015
2	0.55/0.892	3.39/0.093 $\bar{\tau}$ = 1.23[c]	28.4/0.015	0.59/−0.943	6.68/1.000	29.5/0.013
3	1.00/0.896	4.11/0.090 $\bar{\tau}$ = 1.69[c]	28.4/0.014	0.69/−0.959	7.30/1.000	29.3/0.018
4	1.19/0.882	5.20/0.102 $\bar{\tau}$ = 2.10[c]	32.2/0.016	0.90/−0.957	7.20/1.000	29.6/0.022

[a] $I(t) = \sum a_i \exp(-t/\tau_i)$. [b] Fit to biexponential without reconvolution. [c] $\bar{\tau} = \sum a_i \tau_i$.

lene moiety while observation of fluorescence at 340–350 nm yields the kinetics of the monomer fluorescence exclusively. On the basis of the steady-state fluorescence we expect little or no naphthalene excimer fluorescence at wavelengths longer than 400 nm. On the basis of our multiexponential fits (see below) this seems to be the case.

The naphthalene monomer fluorescence in P2VN is well-known to be highly nonexponential by virtue of energy transfer to excimer-forming sites and/or excited chromophore rotation into an excimer configuration. Our anionic P2VN-b polymer also displays nonexponential decay, which was fit to a biexponential function (Table III) for the time range 0–25 ns.

For the samples of P2VN-*b*-VDPA-a the naphthalene fluorescence was shortened and highly nonexponential. For clarification of the role of the very different decay rates a three-exponential decay function was fit simultaneously to data taken on 0–25- and 0–100-ns time scales. An example of this kind of fit is given in Figure 3, and the fitting parameters are given in Table III. While the decay curves are very similar for these samples, the average lifetime

$$\bar{\tau} = \sum a_i \tau_i \qquad (2)$$

is distinctly shorter as one goes from sample 1 to sample 4. χ_t can be calculated from[8]

$$\chi_t = 1 - \bar{\tau}/\bar{\tau}_0 \qquad (3)$$

where $\bar{\tau}_0$ is the average lifetime of the "model compound". Equation 2 is a specific realization of the zeroth moment of the donor fluorescence decay for a multiexponential decay function, and eq 3 is a general relationship.[8,12] The fundametal assumption in eq 3 is that the donor fluorescent state is the sole precursor state of the acceptor fluorescent state. Thus any sensitization of the acceptor must show up as a shortening of the donor fluorescence lifetime. We use the P2VN-b polymer for the values in Table II. The values of χ_t are always less than χ_{ss} except for sample 1. While we do not wish to argue that a three-exponential decay function has any special physical meaning, it has been our experience that calculations of $\bar{\tau}$ are relatively insensitive to the details of the fitting function (i.e., the preexponential factors and lifetimes tend to compensate each other). Thus while our fits are not very sensitive to the exact value of the longest lifetime component (ca. 30 ns), neither is $\bar{\tau}$ because shortening this τ value tends to increase its preexponential factor. However, our value of $\bar{\tau}$ is significantly shortened if we exclude this term from the $\bar{\tau}$ calculation (see Discussion). The most significant uncertainty in the values of χ_t arises from the suitability of P2VN-b as a model compound, since it is known that the rate of excimer formation is dependent on molecular weight and tacticity.[2,10] Phillips et al.[13] presented a high-quality three-exponential fit to monomer decay in free-radical polymerized P2VN. This decay had a major component with 2.1 ns (and $\bar{\tau}$ = 2.4 if the weak, long-lived component (54.6 ns) is ignored, $\bar{\tau}$ = 2.9 ns if it is not). This value for $\bar{\tau}_0$ would reduce our calculated χ_t even more.

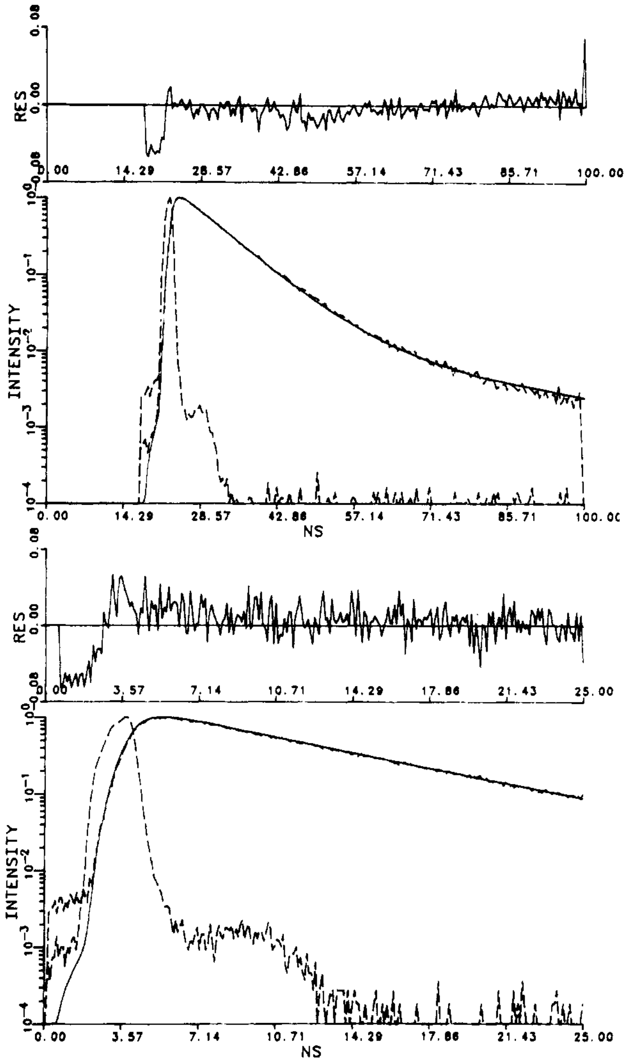

Figure 3. Example of simultaneous fit of fluorescence decay for 25- and 100-ns time range (for P2VN-*b*-VDPA-a, sample 3, λ_{obsd} = 460 nm).

The presence of the long-lifetime component tends to imply the existence of some free P2VN, which was presumably terminated before addition to VDPA. This lifetime is similar to what one would expect for the P2VN excimer. It is known that the excimer is capable of regenerating the monomer state via thermal dissociation. A similar component is observed in the anthracene region (see below).

The time-dependent fluorescence in the anthracene region displays a clear build-up followed by a component with a lifetime in the 6.2–7.2-ns range (Table III). As was mentioned above, there is a minor component with a lifetime of ca. 30 ns, which we ascribe to an underlying naphthalene excimer. The build-up time constant is apparently <1 ns. While close to our time resolution, there does seem to be a systematic variation in the lifetimes along the series of samples. While for simple kinetics the acceptor build-up time should correspond to the fast decay of the donor, the situation is more complex for systems in which the donor also has a complicated decay function. We do not believe the precision of our DPA rise time fit is adequate for detailed comparison to the naphthalene decay.

Discussion

This article has described a novel example of a photon-harvesting block copolymer. There have been a number of reports of polymers in which Förster energy traps have been covalently bound to random sites on the polymer coil[8,14] or, less frequently, as polymer end groups.[15] Our block copolymer is a special case of the latter. While the quantum efficiency (χ) of energy transfer from naphthalene to DPA is very high for the present system, it is not remarkably high considering that the mole fraction of anthracene varies between 0.04–0.10 for the P2VN-*b*-VDPA-a samples (Table II). Values of χ nearly as high have been reported for analogous polymers with approximately 0.01 mole fraction of anthracene. As is intuitively obvious, detailed simulations demonstrate that placement of traps at the ends of polymers is less efficient (per unit trap) in intercepting a migrating excited state than randomly placing traps along the polymer chain. However, with a block polymer one could imagine orienting the polymer such that one kind of segment is in contact with a phase or a solid (e.g., through preferential solubility, miscibility, or adsorption). In this case the unidirectional nature of the sensitization process could be exploited to deliver photon energy to a specific interface over a wide action spectrum. The present system provides one example of the properties of such a copolymer.

The time dependence of the donor–acceptor fluorescence varies very systematically in this series. Increasing the naphthalene/DPA ratio leads to a slight increase in the naphthalene average lifetime and a commensurate increase in the rise time of the sensitized DPA fluorescence. While a detailed discussion of the short-time components is beyond the scope of this paper (and possibly the precision of the data), it does seem clear that the quantum efficiency of sensitization as measured from the time dependence of fluorescence is less than that measured from steady-state spectra (i.e., $\chi_t < \chi_{ss}$). We have encountered this situation previously and have postulated a nonfluorescent precursor state that is common to the naphthalene and DPA emitting state.[8] A similar concept has appeared in a discussion of the photophysics of poly(*N*-vinylcarbazole) by Kauffmann et al.[16] A kinetically equivalent possibility is that some fraction of the energy-transfer process is so fast that we cannot detect it (e.g., so-called "static quenching"). Both these situations may be very common in polymer photophysics.

Finally, we comment that for the present system it is very likely that cross-chain (as opposed to down-chain) energy transfer occurs because of the large Förster R_0 for naphthalene/DPA (ca. 25 Å). It remains to be seen if the relative importance of these two modes of energy transfer could be distinguished from a detailed study of the time-dependent fluorescence. Efforts on this and related problems are currently being pursued.

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Registry No. (2VN)(VDPA) (block copolymer), 114132-43-3.

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