Interblock Electron Transfer in 2-Vinylnaphthalene–((*N*,*N*-Dimethylamino)methyl)styrene Block Copolymers

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ABSTRACT: 2-Vinylnaphthalene–((*N*,*N*-dimethylamino)methyl)styrene block copolymers (**1**) of variable block lengths constituted from two monomers with substantially different redox potentials were prepared by anionic polymerization. Interblock electron transfer studied by fluorescence quenching was most efficient in block copolymers with approximately equal individual block lengths. Copolymers with very different lengths for the individual blocks exhibited substantially lower quenching efficiencies, probably because of interblock phase separation, as suggested by phase-dispersal studies. The intensities of the observed ground-state charge-transfer absorptions in these block copolymers correlate with the degree of phase separation.

Introduction

Controlled electron transfer over supramolecular distances is required for efficient molecular electronic devices such as molecular wires, switches, and memory devices.[1–3] However, difficulties in defining the directionality of electron transfer and preventing back electron transfer within such arrays have made the design of appropriate polymers a continuing scientific challenge. In addition, methods for the assembly of redox-active or photoresponsive molecules into spatially ordered arrays have not yet been adequately developed.

In this study, we have characterized block copolymers prepared from monomers containing groups of differing redox potential. These polymers are interesting as vehicles for characterizing directional electron transfer between blocks and as probes for structural order required for long-distance charge separation.[2] For example, phase-separated block copolymers are known to form ordered micellar, lamellar, or columnar structures in solution or in the solid state,[4–6] producing environments that may be conducive, in principle, to efficient interphase electron exchange. The question to be addressed with our synthetic polymers is whether photophysical measurements can provide useful information on phase separation in redox-functionalized block copolymers and whether block-to-block electron-transfer efficiency is related to polymer morphology.

Experimental Section

Model Compounds. Dimethylbenzylamine (BDMA, 99+%, Aldrich) and naphthalene (Np, 99%, Aldrich) were used as received.

Copolymer Synthesis. Block copolymers with varying ratios of block sizes were prepared by anionic living polymerization[7] in which defined quantities of the desired monomer are sequentially introduced. The monomers employed were commercial samples of 2-vinylnaphthalene (2-VNp, Aldrich, twice sublimed) and ((*N*,*N*-dimethylamino)methyl)styrene (DMS, Mp-Dajac, as a 4:6 *m*:*p* isomeric mixture, distilled from dibutylmagnesium and degassed by three freeze–pump–thaw cycles). These monomers were placed in a Wheaton bottle equipped with a side arm that could store, during the formation of the first block, the monomer to be later introduced as the second block. The bottle was purged of impurities that could quench the polymerization by a preliminary wash with *n*-butyllithium before being charged with the monomers in a N_2-filled drybox. The filled bottle was then transferred to a Schlenk line where the polymerization was conducted under Ar. Polymerization was initiated by the injection of a precisely measured volume of freshly titrated *n*-butyllithium (2.5 M in hexane, Aldrich) to a dry, degassed solution of the first monomer in benzene (distilled from potassium and 0.1 M dibutylmagnesium and degassed by three freeze–pump–thaw cycles). The resulting dark red solution was allowed to stand at room temperature for 35 min. The second monomer was then washed into the reaction bottle and allowed to stand for an additional 30 min, after which the degassed living polymer was quenched by the addition of methanol (0.1 mL), causing the solution to turn pale yellow immediately. The polymer was precipitated upon addition of methanol and was separated by filtration before being dried in a vacuum oven for 4 h at 60 °C.

Polydispersities (PD) for the block copolymers were determined by gel permeation chromatography (GPC) on μ-Styragel to be between 1.07 and 1.30 against a polystyrene standard. Molecular weights were determined by GPC size exclusion and by nuclear magnetic resonance (NMR) end group analysis (M_{NMR}).[8] The GPC analysis gave both the weight-average molecular weight (M_w) and the number-average molecular weight (M_n). However, the GPC analysis was inaccurate for polymers with high DMS loadings because these polymers were only sparingly soluble under standard GPC conditions and trailed badly on standard columns. End-group analysis by NMR spectroscopy was therefore used exclusively in the molecular weight determination of the DMS-rich series. The relative intensity of the NMR signal from six of nine of the protons from the *n*-butyl end groups (δ 0.7–1.2) derived from the initiator was compared with that of the two-proton benzylic signal in the δ 3.1–3.4 range for the DMS block and the seven-proton signal in the δ 6.2–7.8 range for the VNp block. The molecular weight obtained for the 2-vinylnaphthalene oligomer $(2\text{-VNp})_{10}$ by the NMR method corresponded within 5% to the M_w obtained by GPC measurements; for block copolymers of higher DMS content, the M_{NMR} values matched well with the light scattering determinations (Table 1), M_{LS}, which were collected on a DAWN B (Wyatt Technology) multiangle light scattering photometer and converted to molecular weights by Zimm's method.[9] Glass transition temperatures (T_g) of the polymers were measured on a Perkin-Elmer 7500 differential scanning calorimeter. The T_g of $(2\text{-VNp})_{10}$ was significantly lower than that reported in the literature for the 405-mer (132 °C),[10a] probably as a result of lower molecular weight.[10b] T_g for the 33-mer of DMS is very broad, even with highly purified samples, as were the T_g's for all block copolymers containing a relatively long p(DMS) block, probably as a result of a DMS monomer *m*:*p* isomeric mixture.

Poly(2-vinylnaphthalene) (p(2-VNp)) was synthesized as a 10-mer according to literature methods.[7] ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.3–7.8 (br, 7H), 1.7–2.0 (br, 1H), 1.2–1.7 (br, 2H), 0.7–1.5 (br, 0.9H, 0.3H of which overlapped with polymer (δ 1.21–1.5) and 0.6H of which did not (δ 0.7–1.2)), M_{NMR}: 1540 ± 150.

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Table 1. Physical Properties of Various (2-VNp)$_x$(DMS)$_y$ Copolymers

comp[a] (2-VNp)$_x$(DMS)$_y$		mol wt[b]			T_g[c]
x	y	M_{NMR}	PD	M_{LS}	(±5 °C)
10	0	1540	1.11	*d*	95
10	1	1800	1.20	*d*	105
11	3	2200	1.22	*d*	110
10	6	2500	1.28	*d*	broad
9	9	2900	1.28	*d*	broad
9	12	3300	1.28	*d*	broad
11	22	5300	N/A[e]	5500[f]	broad
0	33	5400	N/A[e]	4800[f]	broad

[a] Composition from monomer mixture ratio. [b] Molecular weight determinations: M_{NMR}, end group analysis by nuclear magnetic resonance; PD, polydispersity by gel permeation chromatography (GPC); M_{1S}, Light Scattering data converted to molecular weight by Zimm's method.[9] [c] Glass transition temperature. [d] Measurements were inaccurate because of the weak light scattering from low MW polymers. [e] Polymer trails badly in the GPC column; no data were available. [f] Refractive index increment of the polymer solution, d*n*/d*c* = 0.127, in benzene.

UV (THF): 228 (ϵ = 37 400), 280 nm (ϵ = 3300 M^{-1} cm^{-1}). GPC (polystyrene standards, CH_2Cl_2): M_w, 1520 ± 20; M_n, 1290 ± 20; PD, 1.11. T_g: 95 °C.

Poly[((*N,N*-dimethylamino)methyl)styrene](p(DMS)) was synthesized as a 33-mer.[7c] ^1H NMR (300 MHz, $CDCl_3$): δ 6.3–7.3 (br, 4H), 3.1–3.4 (br, 2H), 2.0–2.3 (br, 6H), 1.7–1.9 (br, 1H), 1.20–1.7 (br, 2H), 0.7–1.5 (br, 0.27H, 0.09H of which overlapped with polymer (δ 1.2–.15) and 0.18H of which did not (δ 0.7–1.2)), M_{NMR}: 5300. UV (THF) 218 (ϵ = 5800), 280 nm (ϵ = 74 M^{-1} cm^{-1}). Broad T_g.

2-Vinylnaphthalene–((*N,N*-dimethylamino)methyl)styrene block copolymers ((2-VNp)$_x$(DMS)$_y$) were synthesized by polymerizing 2-VNp and DMS in varying ratios (0.10–0.20 g). ^1H NMR (300 MHz, $CDCl_3$): δ 6.2–7.8 (br), 3.1–3.4 (br), 2.0–2.3 (br), 1.2–2.3 (br) (integration ratios corresponded to those expected from the monomer mixture to within ±10%), 0.7–1.5 (br). UV (THF): 234 (s), 276 nm (w). NMR and GPC (polystyrene standards, CH_2Cl_2): M_{NMR}, 1500–5400; PD, 1.20–1.30 (Table 1).

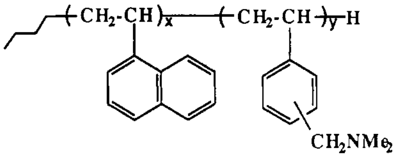
Micelle Formation. Light scattering measurements for the polymers listed in Table 1 were performed on a DAWN B (Wyatt Technology) multiangle light scattering photometer equipped with a He–Ne laser tuned at 632 nm. The normalized excess Rayleigh ratio[9] of the scattered light (at various angles ranging from 23 to 128° from the surface of the solution) was converted to turbidity, which was plotted against polymer concentration to give the critical micellation concentration (cmc) of each copolymer.[9,11–12]

Fluorescence Quenching Measurements. Fluorescence emission spectra were recorded on an SPF-500C spectrofluorometer. Fluorescence intensities of solutions of (2-VNp)$_x$(DMS)$_y$ copolymers and model compounds in degassed, freshly distilled THF or spectroscopic grade methanol or benzene at concentrations between 4×10^{-6} and 4×10^{-7} M, either alone or in the presence of varying concentrations of quencher, were monitored in the 300–500-nm region (maximum emission at 405 nm) upon excitation at 280 nm. Excitation at 280 nm deposits 95–99.8% of incident energy into a naphthalene absorption band; excitation of (DAMS)$_{33}$ at 280 nm gives no fluorescence. The observed naphthalene fluorescence efficiency was corrected for absorption by the p(DMS) block in the block copolymers. All the solutions were deoxygenated by bubbling with dry nitrogen gas for at least 15 min before the fluorescence measurement.

Absorption Measurements. UV absorption spectra of the (2-VNp)$_x$(DMS)$_y$ copolymers were measured on a Hewlett Packard 8451 diode array spectrophotometer in the 200–350-nm region. The absorption spectra of the block copolymers were corrected by subtraction of those of (2-VNp)$_{10}$ and (DMS)$_{33}$ homopolymer mixtures with the same net molar concentrations to obtain difference spectra indicative of residual ground-state charge-transfer absorption. The polymers were studied in the concentration range of 7×10^{-7}–3×10^{-6} M, where intermolecular association had been shown to be negligible. Transient absorption spectra of (2-VNp)$_x$(DMS)$_y$ copolymers were recorded on a conventional laser flash photolysis unit that uses a Quantel Nd:YAG laser (266 nm, 25 mJ, 15-ns pulse width) as the excitation source, at the Center for Fast Kinetics Research at the University of Texas at Austin, in which signal intensity is monitored with a Biomation 8100 transient recorder in the 300–700-nm region. The copolymer solutions were outgassed in situ by bubbling with dry nitrogen for 15 min before and throughout the experiment.

Results and Discussion

Polymer Synthesis. Copolymers 1 comprising blocks derived from 2-vinylnaphthalene and from ((*N,N*-dimethylamino)methyl)styrene (as a 4:6 mixture of *m* and *p* isomers) were prepared by anionic polymerization. Copolymers with a fixed 2-VNp block length and a variable DMS block length were synthesized to study the influence of polymer morphology on electron-transfer efficiency between blocks. Table 1 shows that (2-VNp)$_{9-11}$(DMS)$_y$ (y = 1, 3, 6, 9, 12, and 22) block polymers were obtained with relatively low polydispersities and expected molecular weight ranges.



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Phase Dispersal of Copolymer 1. A unique characteristic of block copolymers is their tendency for phase separation.[4–6] The incompatibilities of the individual blocks comprising the polymer, as reflected in microphase separation in the solid state and in concentrated solution and in their different solubilities in polar and nonpolar solvents, lead to structures in which unlike copolymer sequences are microseparated.[6] Styrene–((*N,N*-dimethylamino)methyl)styrene block copolymers have been reported to form a phase-separated lamellar structure in the solid state because of the contrasting polarities of the nonpolar aromatic and polar dimethylbenzylamine blocks.[5] Styrene–methyl methacrylate block copolymers are known to form micelles in toluene/furfuryl alcohol, because furfuryl alcohol is a selective solvent for polystyrene.[6c]

Copolymer 1 forms an inverse micelle in benzene/methanol because methanol serves as a selective solvent to dissolve (DMS)$_{33}$ but precipitates (2-VNp)$_{10}$. In contrast, benzene solubilizes (2-VNp)$_{10}$ and stabilizes micelle formation. The presence of a stable, compact, micelle in solution of 1 is indicated by a bluish, turbid appearance (lasting 1 month or longer) and high molecular weight (ca. 10^5–10^6, ~300–500 unimers per micelle) when measured by light scattering, with an aggregated assembly of ~30–50 nm.

Critical Micellation Concentration (cmc) of the Block Copolymers 1. The (2-VNp)$_{11}$(DMS)$_{22}$ and (2-VNp)$_9$(DMS)$_9$ block copolymers were examined as probes for micellation in benzene/methanol mixtures of varying composition. The onset of light scattering with (2-VNp)$_{11}$(DMS)$_{22}$ in 6:5 (by volume) benzene/methanol occurred at a concentration of 9.1×10^{-6} M. With lower ratios of benzene to methanol, the copolymer was insoluble, whereas with more benzene-rich solvent mixtures (compositions greater than 2:1), no micellation could be observed (a nonscattering homogeneous solution was observed for all polymer concentrations between 10^{-7} and 10^{-1} M). By similar methods, the (2-VNp)$_9$(DMS)$_9$ block copolymer in 3:1 benzene/methanol was shown to have a cmc of 1.7×10^{-5} M, with either precipitation or a completely

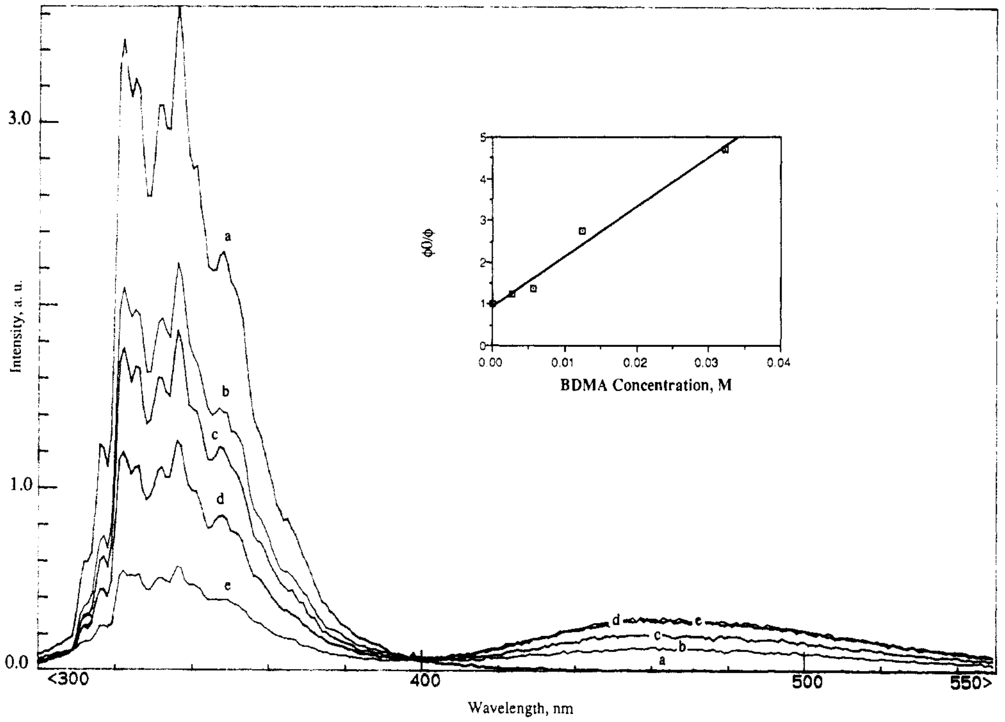

Figure 1. Fluorescence quenching spectra of naphthalene as a 1.8 × 10^{-5} M solution in deoxygenated THF by dimethylbenzylamine (BDMA) at different BDMA concentrations: (a) 0; (b) 2.5 × 10^{-3} M; (c) 5.0 × 10^{-3} M; (d) 1.2 × 10^{-2} M; (e) 3.2 × 10^{-2} M. Excitation wavelength, 280 nm. Inset: Stern–Volmer plot for the fluorescence quenching.

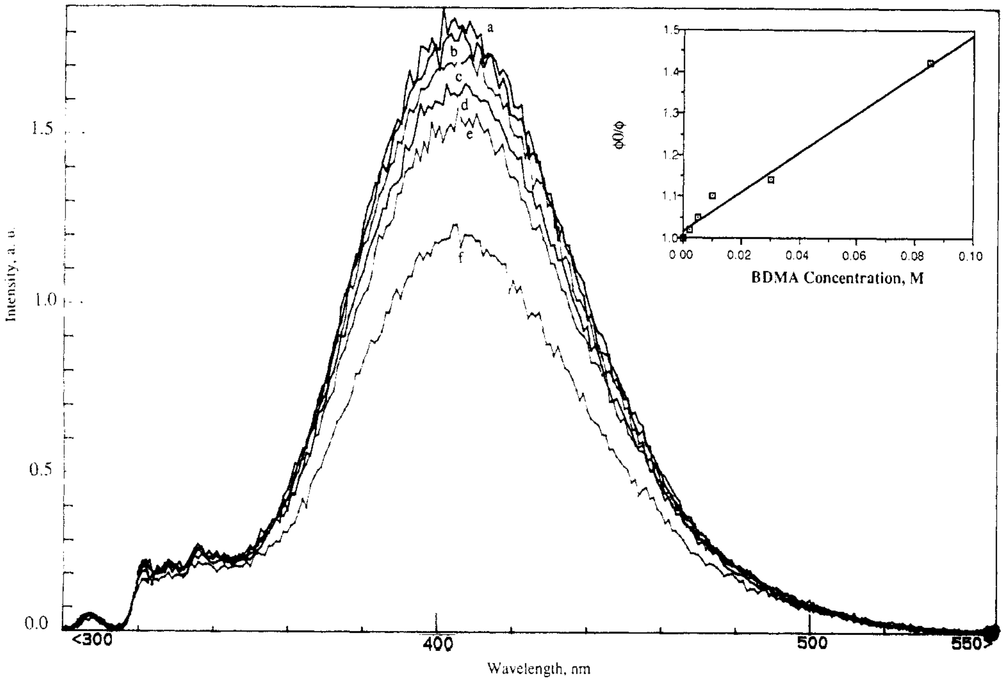

Figure 2. Fluorescence quenching spectra of $(2\text{-VNp})_{10}$ as a 1.4 × 10^{-6} M solution in deoxygenated THF by dimethylbenzylamine (BDMA) at different BDMA concentrations: (a) 0; (b) 2.6 × 10^{-3} M; (c) 5.3 × 10^{-3} M; (d) 1.0 × 10^{-2} M; (e) 3 × 10^{-2} M; (f) 8.5 × 10^{-2} M. Excitation wavelength, 280 nm. Inset: Stern–Volmer plot for the fluorescence quenching.

homogeneous solution being observed with solvent mixtures of appreciably different composition.

Model Studies. Excited naphthalene (Np) is quenched by dimethylbenzylamine (BDMA) (Figure 1). Literature results suggest that quenching of naphthalene by triethylamine involves electron transfer and that energy transfer (singlet or triplet) is thermodynamically forbidden.[13] A Np–BDMA exciplex emission at 460 nm is observed at high BDMA concentration, as is consistent with strong charge-transfer interactions between singlet excited aromatic hydrocarbon and various amines.[14] Stern–Volmer analysis shows that the rate constant for quenching of monomer fluorescence, k_q, is 1.26 × 10^9 M^{-1} s^{-1}, assuming 96 ns as the Np monomer singlet lifetime.[15]

Fluoresence of the excited $(2\text{-VNp})_{10}$ homopolymer shows only excimer emission (Figure 2). Quenching by BDMA occurs with a rate constant of 1.6 × 10^8 M^{-1} s^{-1}, assuming an excimer lifetime of 30 ns.[16] Thus, the efficiency of excimer quenching is substantially lower than that for the monomer, as has been reported in the quenching of pyrene and anthracene excimers by triethylamine.[17] However, no Np–DMBA exciplex emission could be observed, even at the highest amine concentration employed.

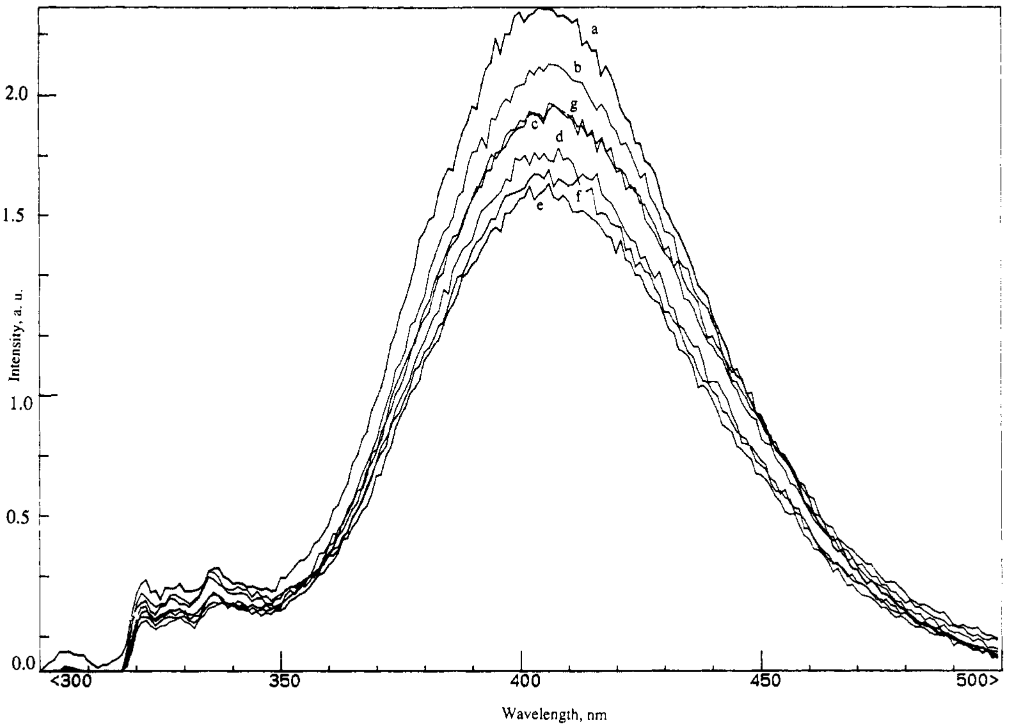

Figure 3. Comparison of fluorescence intensities of $(2\text{-VNp})_{10}$ and block copolymers 1 (a) $(2\text{-VNp})_{10}$; (b) $(2\text{-VNp})_{10}(\text{DMS})$; (c) $(2\text{-VNp})_{11}(\text{DMS})_3$; (d) $(2\text{-VNp})_{10}(\text{DMS})_6$; (e) $(2\text{-VNp})_9(\text{DMS})_9$; (f) $(2\text{-VNp})_9(\text{DMS})_{12}$; (g) $(2\text{-VNp})_{11}(\text{DMS})_{22}$. The concentrations of all the polymers are adjusted to the same optical density at 280 nm (0.052 au) in the range from 4.8×10^{07} to 1.6×10^{-6} M in deoxygenated THF; excitation wavelength, 280 nm.

Table 2. Fluorescence in 2-VNp–DMS Block Copolymers

polymer	ϕ_f/ϕ_{f0} (±0.02)[a,b]
$(2\text{-VNp})_{10}$	1.00
$(2\text{-VNp})_{10}(\text{DMS})$	0.89
$(2\text{-VNp})_{11}(\text{DMS})_3$	0.87
$(2\text{-VNp})_{10}(\text{DMS})_6$	0.84
$(2\text{-VNp})_9(\text{DMS})_9$	0.81
$(2\text{-VNp})_9(\text{DMS})_{12}$	0.82
$(2\text{-VNp})_{11}(\text{DMS})_{22}$	0.89

[a] Ratio of the integrated area under each fluorescence curve of the block copolymer to that of $(2\text{-VNp})_{10}$ from 300 to 500 nm. [b] Average of the fluorescence integrated areas of two independently prepared polymers.

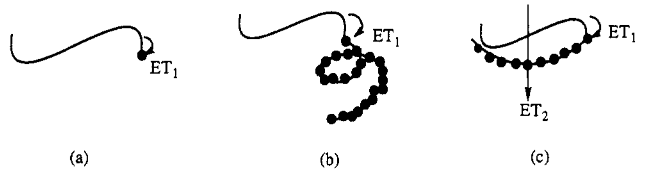

Figure 4. Schematic representation of possible phase dispersal of block copolymers 1 in solution: (a) $(2\text{-VNp})_{10}(\text{DMS})$; (b) phase-separated $(2\text{-VNp})_{11}(\text{DMS})_{22}$; (c) conformationally folded $(2\text{-VNp})_9(\text{DMS})_9$. Solid line, $(2\text{-VNp})_{10}$ block; dots, $(\text{DMS})_y$ block. ET$_1$, electron transfer at the block interface; ET$_2$, electron transfer through direct contact of the pendent groups.

Photophysics of Copolymer 1. Figure 3 displays fluorescence spectra of several block copolymers with a fixed length of the 2-VNp block and variable lengths of the DMS block. As with $(2\text{-VNp})_{10}$ homopolymer, only excimer emission could be observed. Surprisingly, the intensity of emission did not vary monotonically with the length of the DMS block. The integrated fluorescence intensities of the $(2\text{-VNp})_{10}(\text{DMS})_{1\text{-}22}$ complexes are summarized in Table 2, where ϕ_f/ϕ_{f0} represents the corrected ratio of fluorescence intensities of the block copolymers to that of the $(2\text{-VNp})_{10}$ homopolymer at the same concentration when excited into the 280-nm naphthalene absorption band. Figure 3 and Table 2 show that fluorescence efficiency is dependent on the length of the DMS block, with optimal quenching being observed when the two blocks are of approximately the same length. The fluorescence quenching in the block copolymers is similar to the quenching of the excited $(2\text{-VNp})_{10}$ homopolymer by BDMA as shown in Figure 2, reducing the intensity of excimer quenching. Because the rate constant of excimer quenching of the model system is substantially lower than diffusion control[18] in THF at room temperature, only 10–20% fluorescence quenching efficiency was observed in these block copolymers.

With the copolymer containing blocks of very different lengths $(2\text{-VNp})_{11}(\text{DMS})_{22}$, the quenching efficiency is virtually identical to that of $(2\text{-VNp})_{10}(\text{DMS})$. This observation suggests that the quenching mechanism in $(2\text{-VNp})_{11}(\text{DMS})_{22}$ might be similar to that in $(2\text{-VNp})_{10}(\text{DMS})$. In the latter copolymer, quenching must take place at the 2-VNp and DMS block interface, a result that might be similar to that expected if intramolecular phase separation were to occur in $(2\text{-VNp})_{11}(\text{DMS})_{22}$, as shown schematically in Figure 4b). In contrast, the maximum quenching in polymers with more nearly equal block lengths, i.e., $(2\text{-VNp})_9(\text{DMS})_9$, might suggest an additional mode for fluorescence quenching. If quenching could occur either at the block interface or by direct interaction of the redox-active pendant groups brought into contact in a conformation in which the polymer dynamically folded on itself (Figure 4c), more efficient charge-transfer interaction would result. The additional quenching could occur either by dynamic folding or by preequilibration in a ground-state conformation.

Absorption Studies. Difference absorption spectra of $(2\text{-VNp})_{9\text{-}11}(\text{DMS})_y$ (y = 1, 3, 6, 9, and 22) (compared with the sum of the homopolymers $(2\text{-VNp})_{10}$ and $(\text{DMS})_{33}$ with the same monomer compositions and molarities) show an extra broad, red-shifted and tailing absorption ca. 240 and 260 nm (Figure 5). The intensity of this extra absorption is 25–70 times weaker than the $(2\text{-VNp})_{10}$ absorption at 280 nm but is of comparable intensity to that of the $(\text{DMS})_{33}$ absorption (Table 3). This extra

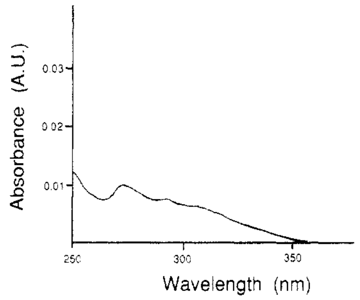

Figure 5. Difference absorption spectrum of $(2\text{-VNp})_{10}(\text{DMS})_9$ and $(2\text{VNp})_{10}$ and $(\text{DMS})_{33}$ at equivalent chromophore concentrations at 10^{-6} M deoxygenated solutions in THF.

Table 3. Ground-State Charge-Transfer Absorption in $(2\text{-VNp})_{9-11}(\text{DMS})_{1-22}$ Block Copolymers

polymer	rel int (%, ±0.2)[a,b]
$(2\text{-VNp})_{11}(\text{DMS})$	<0.5
$(2\text{-VNp})_{11}(\text{DMS})_3$	1.5
$(2\text{-VNp})_{10}(\text{DMS})_6$	2.8
$(2\text{-VNp})_9(\text{DMS})_9$	3.9
$(2\text{-VNp})_9(\text{DMS})_{12}$	2.5
$(2\text{-VNp})_{11}(\text{DMS})_{22}$	2.1

[a] Relative intensity of the integrated area of charge-transfer absorption from 260 to 320 nm in the difference spectra obtained by correction for absorption by parent homopolymers [$(2\text{-VNp})_{10}$ and $(\text{DMS})_{33}$] at concentrations that produce the same absorptivity at 240 nm. [b] Average of the charge-transfer absorption intensities of two independently prepared polymers.

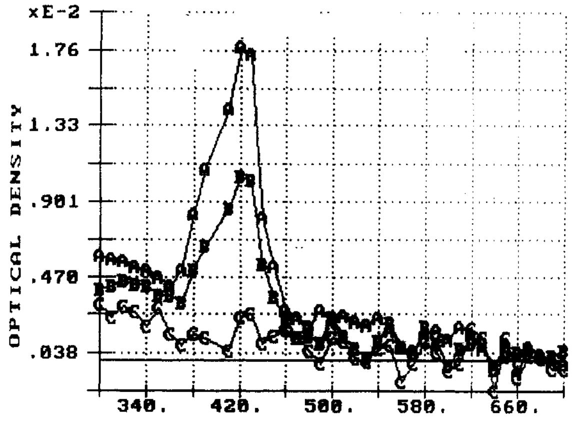

Figure 6. Transient absorption spectrum of $(2\text{VNp})_{10}(\text{DAMS})_6$ as a 1.1×10^{-5} M solution in deoxygenated THF; excitation wavelength, 266 nm. Delay times after flash excitation: (A) 12 ms; (B) 24 ms; (C) 153 ms.

absorption is ascribed to a DMS-to-2-VNp ground-state charge-transfer absorption because of its red shift and low intensity.[19] Ground-state charge-transfer complexation requires that the naphthalene and dimethylbenzylamine blocks be in direct contact, which is maximal in $(2\text{-VNp})_9(\text{DMS})_9$. The extra absorption is consistent with this model, with the intensity being increased with the DMS block length and reaching a maximum in $(2\text{-VNp})_9(\text{DMS})_9$. The intensity of this band correlates directly with the efficiency of fluorescence quenching in these same polymers (Figure 3).

A transient absorption spectrum obtained several microseconds after flash excitation of $(2\text{-VNp})_{10}(\text{DMS})_6$ is shown in Figure 6. A strong absorption at 420 nm is assigned to the naphthalene triplet,[20] produced by back electron transfer before the first measurement.[13a-c] A shoulder absorption at 320 nm is assigned to the naphthalene anion absorption.[13a,21] The DMS cation, however, could not be detected, presumably because of its weak absorption and low lifetime.[13a] The anion yield is ca. 1%, assuming a value of 1500 M^{-1} cm^{-1} as the naphthalene anion extinction coefficient.[21] Back electron transfer seems to be a dominant relaxation mode for the charge-separated species formed in this system. Phase separation does not lead to an appreciably longer-lived charge-separated state than is observed in lower molecular weight donor–acceptor pairs.

Table 4. Micellation Effect on Fluorescence Quenching

polymer	benzene/ methanol (by vol)	concn (M)	ϕ_f/ϕ_{f0} (±0.02)	cmc, M
$(2\text{VNp})_9(\text{Dams})_9$	3:1	2.5×10^{-6} [a]	0.85	1.7×10^{-5}
		2.4×10^{-5} [b]	0.91	
$(2\text{VNp})_{11}(\text{Dams})_{22}$	6:5	2.1×10^{-6} [a]	0.91	9.1×10^{-6}
		1.2×10^{-5} [b]	0.91	

[a] Below cmc for this solvent. [b] Above cmc for this solvent.

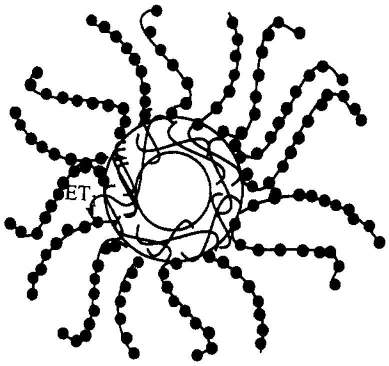

Figure 7. Schematic representation of a phase-separated micelle of $(2\text{-VNp})_9(\text{DMS})_9$. ET_1, electron transfer at the phase-separated block interface.

Effect of Phase Separation on Polymer Photophysics. The efficiencies of excimer fluorescence in $(2\text{-VNp})_{11}(\text{DMS})_{22}$ and $(2\text{-VNp})_9(\text{DMS})_9$ above and below their cmc's are summarized in Table 4. Micellation of $(2\text{-VNp})_{11}(\text{DMS})_{22}$ does not influence the observed fluorescence efficiency, as would be expected if $(2\text{-VNp})_{11}(\text{DMS})_{22}$ exists as a phase-separated structure (Figure 4b) in both homogeneous solution and the micelle. In contrast, micellation of $(2\text{-VNp})_9(\text{DMS})_9$ induces a small but reproducible reduction in excimer fluorescence efficiency, implying the disruption of some quenching mode by micellation. Although the ground-state charge-transfer absorption spectra suggest that $(2\text{-VNp})_9(\text{DMS})_9$ exists in a conformation in which the two blocks are folded onto each other (Figure 4c), micellation must induce phase separation, extending the polymer chain and producing separated nonoverlapping regions for the individual blocks, as shown schematically in Figure 7. In this arrangement, the principal quenching would take place at the interface between blocks, with comparable efficiency as is observed for $(2\text{-VNp})_{10}(\text{DMS})$ and $(2\text{-VNp})_{11}(\text{DMS})_{22}$ in homogeneous solution. This explanation is corroborated by a significant decrease in the intensity of the ground-state charge transfer found for $(2\text{-VNp})_9(\text{DMS})_9$ in the micellar aggregate compared with the same compound in the same solvent at a concentration below its cmc.

Conclusions

The fluorescence efficiency in 2-vinylnaphthalene–((*N*,*N*-dimethylamino)methyl)styrene (1) block copolymers in solution is dependent on polymer composition and chain morphology in solution. For block copolymers with a comparable block length for the two monomers, fluorescence quenching is maximized because of direct ground-state contact, as revealed in the intensity of ground-state charge-transfer absorption. However, for polymers of sufficiently long individual block length to permit phase separation or upon forming of phase-separated micelles, the fluorescence efficiency was substantially increased from the minimum value. The reason for a lower electron-transfer quenching (higher fluorescence efficiency) upon phase separation is the reduction in the degree of direct contact between the donor and acceptor blocks, restricting the efficiency of electron transfer to the weakly interacting block-block interface.

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