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Photoinduced Charge Separation and Photophysical Dynamics in Polynorbornene Chromophore Labeled and Quencher-Labeled Block Copolymers

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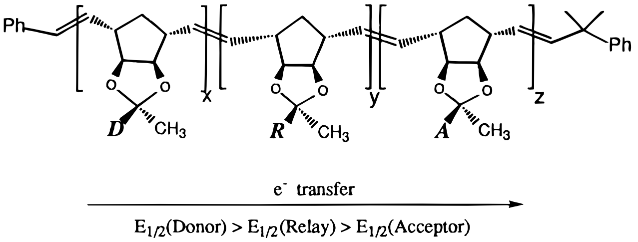
Abstract: Photophysical measurements have been used to characterize a series of well-defined block copolymers labeled with aromatic chromophores and quenchers. These include measurements of (1) energy migration kinetics in the homopolymers and diblock copolymers; (2) solvent effects (CH_2Cl_2, THF, THF/CH_3CN and $CHCl_3$) on exciplex emission in the diblock copolymers; (3) temperature effects on the fluorescence and phosphorescence of the diblock copolymers; (4) the dependence of the efficiency of steady-state and time-resolved emission in several triblock copolymers (dicyanobenzene)$_5$−(phenanthrene)$_n$−(dimethylaniline)$_5$ on relay length (n); and (5) transient absorbance and photoinduced charge separation in these triblock copolymers as a function of relay length. A photoinduced charge separation of 7.2 μs was achieved in a polynorbornyl triblock copolymer bearing a graded series of electron transfer relays: (dicyanobenzene)$_5$−(phenanthrene)$_{10}$−(dimethylaniline)$_5$.

Introduction

A common characteristic of photosynthesis and optoelectronic devices is the light-induced production of a charge-separated ion pair.[1,2] A substantial effort has been made to study this process because it is a key step in catalyzing organic redox reactions[3] and in converting incident light into electrical or optical responses.[4] Attempts to mimic such charge separations in molecular assemblies bearing photosensitizers and electron transfer quenchers have met with impressive success.[5−12] An inherent limitation, however, in achieving long-lived charge separation in such low molecular weight models is that rapid back electron transfer often takes place as a consequence of the typically small spatial separation between the attached donor and acceptor.

An alternative approach to this problem is to use extended block copolymers bearing photoactive groups and redox relays. Substituted polynorbornenes produced by ring-opening metathesis polymerization (ROMP) have rigid backbones onto which can be assembled a series of chromophores and quenchers suitable to induce long-distance photoinduced electron transfer. With these molecules, we are able to study energy migration to the block interfaces where electron transfer produces an ion pair. Electron hopping through the block can then lead to substantial spatial separation of the newly formed counterions. By varying the conditions (temperature and solvent) under which the polymers are excited, specific excited states can be accessed.

The polymers described in this paper have the following general structure, where D designates an electron donor, A an electron acceptor, and R an electron transfer relay which, upon photoexcitation, shuttles energy or electrons between D and A.



These groups are positioned so as to provide a directional redox gradient for the desired electron transfer between the component blocks. The subscripts *x*, *y*, and *z*, which define the number of repeat units in each block, can be varied to control the distance between the donor and acceptor blocks. Unidirectionality of electron transfer shuttling is ensured by a positive driving force derived from the redox potentials of the appended groups.

In a preliminary communication, we have reported the synthesis and steady-state fluorescence of several of these block copolymers prepared by ROMP of monomers **I**[13,14] (Chart 1). Homopolymers **II** were shown to be sufficiently conformationally regular and inflexible to impede excimer formation between

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[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

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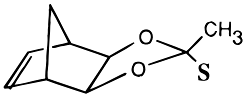
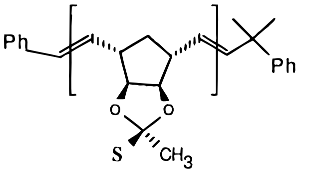
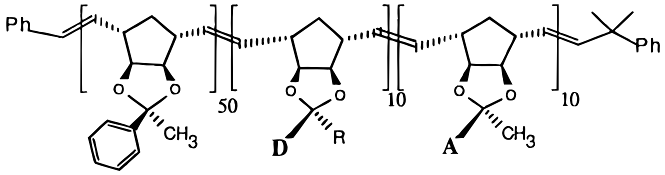
Chart 1



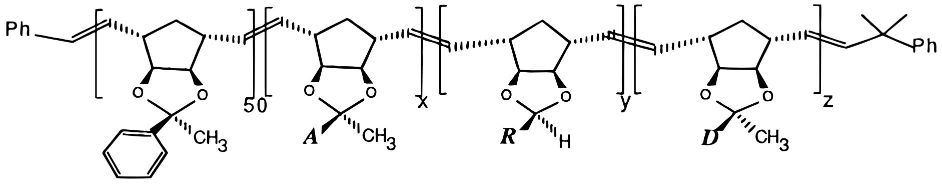
Ia, S = 2-naphthyl
Ib, S = 3-phenanthryl
Ic, S = 2-anthryl



IIa, S = 2-naphthyl
IIb, S = 3-phenanthryl
IIc, S = 2-anthryl



IIIa, A = 2-naphthyl, D = 3-(N,N-dimethylanilino), R = CH_3
IIIb, A = 3-phenanthryl, D = 3-(N,N-dimethylanilino), R = CH_3
IIIc, A = 2-anthryl, D = 3-(N,N-dimethylanilino), R = CH_3
IIId, A = 2,5-dicyanophenyl, D = 3-phenanthryl, R = H



IVa: **A**=2,5-dicyanophenyl, x=5, **R**=3-phenanthryl, y=10, **D**=3-(N,N-dimethylanilino), z= 5
IVb: **A**=2,5-dicyanophenyl, x=5, **R**=3-phenanthryl, y=5, **D**=3-(N,N-dimethylanilino), z= 5
IVc: **A**=2,5-dicyanophenyl, x=5, **R**=3-phenanthryl, y=2, **D**=3-(N,N-dimethylanilino), z= 5
IVd: **A**=2,5-dicyanophenyl, x=5, **R**=3-phenanthryl, y=1, **D**=3-(N,N-dimethylanilino), z= 5

pendent chromophores. Block copolymers **III** are required in order to observe energy migration to the block interface, ultimately producing exciplex emission. An initial block of redox inactive polymer derived from the ketal of acetophenone in copolymers **III** had no effect on the observed photophysics, but instead improved block copolymer monodispersity. This initial block allows us to focus on the effect of variation of chain length in the photoactive segment by minimizing the synthetic importance of the ROMP initiation step.[14] By comparing copolymers **III**, bearing a single electron donor D and an electron acceptor pair A with copolymers **IV** containing a third absorptive relay spacer R of variable length between the D and A blocks, we were able to show that exciplex emission occurred by exciton migration to the interface, rather than by polymer folding.[13] In this paper, we thoroughly describe the photophysical properties of a complete family of block copolymers **III** and **IV**. Photophysical measurements of the following five types were made: (1) energy migration kinetics; (2) solvent effects on exciplex emission in **III**; (3) temperature effects on fluorescence and phosphorescence emission in **III**; (4) steady-state and time-resolved emission in **IV** as a function of relay length; and (5) spectral monitoring of transient absorption and photoinduced charge separation in **IV** as a function of relay length.

Experimental Section

Materials. Spectrophotometric grade methylene chloride (CH_2Cl_2), tetrahydrofuran (THF), and acetonitrile (CH_3CN) were used as received for fluorimetry. Chloroform ($CHCl_3$) was purchased as spectrophotometric grade and stored over anhydrous K_2CO_3 prior to use. 2-Methyltetrahydrofuran (MTHF) was heated to reflux over sodium and fractionally distilled immediately before use. The syntheses of all polymers used in the photophysical studies were reported previously.[14]

Fluorescence Spectra. Emission and excitation spectra were recorded at 25 °C in CH_2Cl_2, THF, CH_3CN, or $CHCl_3$, or at 77 K in a MTHF glass, by using a SLM Aminco SPF 500 spectrofluorimeter. All solutions were deoxygenated by bubbling with nitrogen and had OD < 0.10 in a 1-cm cuvette, unless otherwise noted. The emission spectra were measured in the ratio mode (to correct for variations in lamp intensity with time). Delayed fluorescence and phosphorescence spectra were recorded with a phosphoroscope attachment that uses light baffles and a variable-speed chopper (0−10 000 rpm). Stern−Volmer quenching constants were measured by monitoring the decrease in fluorescence intensity at the emission maximum upon adding carbon tetrachloride.

Temperature-Dependent Spectra. All temperature-dependent spectra were measured in deoxygenated MTHF cooled to a glass in liquid nitrogen at 77 K. In this work, an air-saturated solution of polymer in MTHF was bubble degassed with nitrogen prior to cooling to 77 K. To prevent light scattering of the excitation wavelength from the low-temperature Dewar flask, a 350-nm cutoff filter was inserted at the front of the emission monochromator.

Fluorescence Lifetimes. Fluorescence decays were recorded via time-correlated single-photon counting.[20] The light source was a Photochemical Research Associates (PRA) Model 510B thyratron-gated flash lamp operated at 20 kHz, 5 kV, and 0.5 atm of air. The flash lamp had a full width at half-maximum of ca. 4 ns. The excitation wavelength was selected with two Jobin-Yvon monochromators.

Transient Absorption Spectra. Flash photolysis studies were made with a Q-switched, frequency-tripled ($\lambda = 355$ nm, 30 mJ) Quantel YG481 Nd:YAG laser (pulse width 12 ns). A right-angle geometry was used to obtain transient absorption signals from a 1-cm cell with solutions of OD $= 0.2-0.4$. An averaging procedure was used to increase the signal-to-noise ratio in which the signals from 30 laser pulses were averaged for each absorption decay measurement. The formation and decay of transients were monitored by optical absorption

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[20] O'Connor, D. V., Phillips, D., Eds. *Time-correlated Single Photon Counting*; Academic Press: New York, 1984.

spectroscopy, with spectra being recorded at each wavelength emitted by a pulsed high-intensity Xe arc lamp (150-W probe). The spectra were obtained by recording the absorbance changes at 5- or 10-nm increments with five to seven laser pulses being averaged at each wavelength on in-house software at the Center for Fast Kinetics Research.

Results and Discussion

A. Energy Migration in Homopolymers II and Block Copolymers III. The intramolecular hopping of electronic excitation energy along a consecutive chain of light-absorbing chromophores is known as energy migration.[15] In our block copolymers, such transfers are useful for transporting light absorbed anywhere along the block to an adjacent block bearing one or more pendent quenchers. At the interface between the blocks, excited-state electron transfer can take place to produce either a charge-stabilized exciplex or a charge-separated ion pair.[16]

Experimentally, energy hopping can be studied in two ways: directly, by fitting the rise times obtained from time-resolved exciplex emission measurements of the labeled diblock copolymers bearing suitable chromophores and quenchers;[17] or indirectly, by comparing rates of Stern−Volmer fluorescence quenching of the corresponding homopolymers, where no excimer or exciplex emission can be seen.[18] The time-resolved emission of the monomers **Ia**−**c** and the corresponding homopolymers **IIa**−**c** displayed single exponential decay curves with excited-state lifetimes of 8.2, 16, and 4.2 ns, respectively.[13,14] The block copolymers **IIIa**−**d** were analyzed for energy hopping by each of these methods.

Direct measurement of the time-resolved decay of intermolecular exciplexes between poly(vinylarenes) and dimethylaniline shows an initial growth (rise), followed by an exponential decay.[18] The rise component is indicative of rapid singlet-excited-state energy migration from the initial site of photoexcitation to the site where exciplex or excimer formation takes place.[18] In Figure 1 are shown the time-resolved emission spectra of **IIIa**−**IIIc**. These curves were obtained by exciting **III** at the indicated excitation wavelength (λ_{ex}) and by monitoring the emission at the maximum (λ_{ex}) of the intramolecular exciplex emission observed in steady-state measurements. The rise times for the exciplex emissions from **IIIa** and **IIIb** could be observed easily on a time scale of several nanoseconds, but that for **IIIc** could not be observed on a nanosecond laser. We therefore assume that energy migration takes place in less than 1 ns, probably because of the short lifetime of the anthracene singlet excited state. On this shorter time scale, small discontinuities in the decay curve are amplified significantly. Hence, **IIIc** shows a small residual as part of its decay.

The singlet energy migration rates in **IIIa**−**c** were obtained by fitting the curves to the function $I(t) = Sa_i \exp(-\tau/\tau_i)$.[19] From the resulting fits listed in column one of Table 1, the initial rise time τ is assigned as needed for formation of an intramolecular exciplex. This value is then used to obtain the rate of energy migration required to produce the observed exciplex. The fitted lifetimes of the rise, along with the rates of exciplex formation, are summarized in Table 1. The rates of exciplex formation thus obtained are comparable to those available in the literature for analogous systems.[17] The migration rate for **IIIc** is more than an order of magnitude faster than those for **IIIa** and **IIIb**.

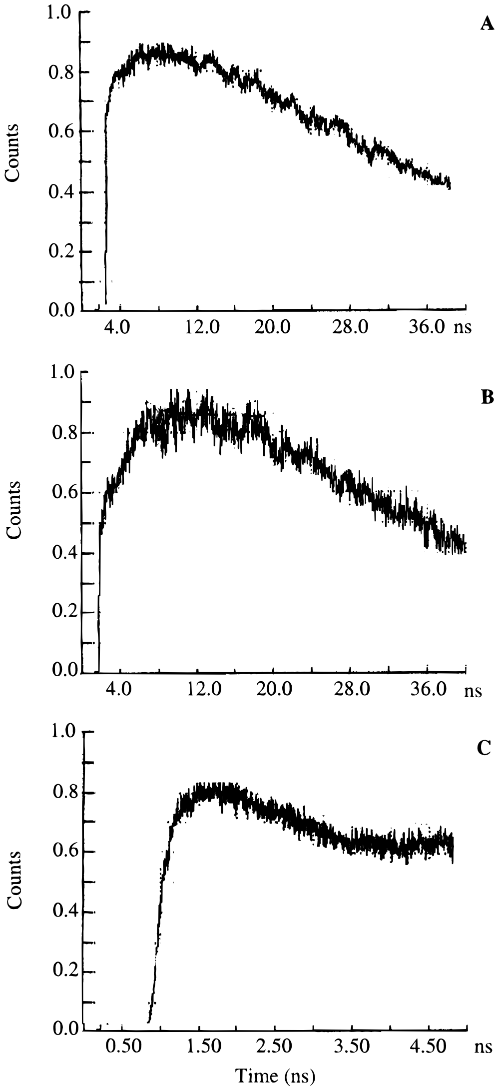

Figure 1. Time-resolved emission rise times as 10^{-5} M solutions in THF: (A) **IIIa** at $\lambda_{em} = 430$ nm, $\lambda_{ex} = 284$ nm, $\tau = 7.0$ ns; (B) **IIIb** at $\lambda_{em} = 460$ nm, $\lambda_{ex} = 355$ nm, $\tau = 8.3$ ns; and (C) **IIIc** at $\lambda_{em} = 520$ nm, $\lambda_{ex} = 355$ nm, $\tau = 0.27$ ns.

Table 1. Rise Times for Exciplex, Rates of Exciplex Formation, and Distances between Chromophores in **III**[a]

diblock copolymer	τ: exciplex rise time (ns) ($\pm$0.1)	rate of energy migration (s^{-1}) $\times 10^{-8}$	R_0 Förster radius for self-transfer (Å) $\pm$ 0.1 Å	distance between chromophores (Å) $\pm$ 0.1 Å
IIIa	7.0	1.4	7.3	7.2
IIIb	8.3	1.2	8.8	7.9
IIIc	<1	37	22	14

[a] The transient emission spectra were measured in degassed THF as 10^{-5} M solutions at room temperature. The fitted rise times from these transients were used for the calculation of the reported data.

Additional information can be obtained from the rise time in copolymers **III** if we assume a Förster mechanism for the energy migration.[17] For example, the time required for energy hopping between adjacent chromophores can be used to obtain a distance between adjacent chromophores along the polymer backbone. The time constant for energy hopping (τ_h) between adjacent chromophores is given by eq 1,[17] in which τ is the singlet-

$$\tau_h = \tau(R/R_0)^6 \tag{1}$$

excited state lifetime of the pendent chromophores, R is the distance between adjacent chromophores, and R_0 is the Förster radius separating like chromophores.[21] The results of these calculations, given in the last column of Table 1, show the

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(21) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469−1482.

(22) Turro, N. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991.

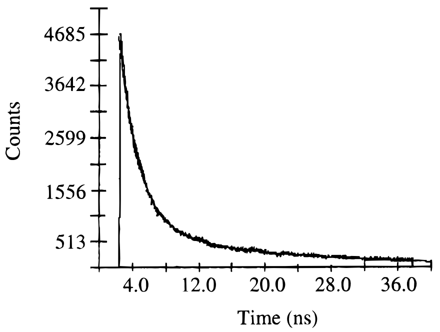

Figure 2. Time-resolved emission decay curve of **IIId** at $\lambda_{em} = 460$ nm, $\lambda_{ex} = 355$ nm, with biexponential fit: $\tau_1 = 2.4$ ns, $\tau_2 = 18$ ns.

Table 2. Excitation Diffusion Lengths (Λ_s) from Stern−Volmer Fluorescence Quenching of Homopolymers **IIa**−**c** and Their Corresponding Monomers

polymer/monomer	$k_q\tau_0{}^a$ (M^{-1})	$\tau_0{}^b$ (ns)	Λ_s/D^c	Λ_s (Å)
IIa	2700	8.2	1.5	56
Ia	2400	8.2		
IIb	200	16	2.0	97
Ib	100	16		
IIc	300	4.2	0.25	18
Ic	400	4.2		

[a] Calculated from the slope of a Stern−Volmer quenching (CCl_4) plot. [b] Lifetimes determined from single photon counting experiments, using the fit obtained from a single exponential decay curve. Emission measured in degassed THF as a 10^{-5} M solution. [c] Calculated using eq 3.

greatest distance between chromophores to be encountered in the anthracene-containing polymer **IIIc**, 14 Å.

In contrast to **IIIa**−**c**, **IIId** shows no rise in emission intensity. Instead, the observed transient decays smoothly by a biexponential with decay times of 2.4 and 18 ns, respectively, Figure 2. We assign the 2.4-ns component to energy migration/exciplex formation, which is parallel to that observed in **IIIa**−**c**. Because we observe from **IIId** steady-state exciplex emission at a level greater than the 10% intensity expected from stoichiometric interactions taking place only at the interface,[13] we know that energy migration must take place. The lack of a resolvable rise time is therefore indicative of very fast (subnanosecond) energy migration to the block interface. Hence, energy migration rates could not be analyzed in **IIId** in the same way as for **IIIa**−**c**.

An indirect method for the analysis of energy migration in end-labeled polymers has been described by Webber and coworkers.[18] By comparing the rates of Stern−Volmer quenching of chromophore-labeled homopolymers (**IIa**−**c**) and their respective monomers (**Ia**−**c**, eq 2), energy migration rates and excitation diffusion lengths were obtained, Table 2, using equations derived previously.[17] The quenching rate is obtained from the Stern−Volmer equation, eq 2,[21] in which k_q is the rate

$$I_0/I_Q = 1 + k_q\tau_0[Q] \qquad (2)$$

constant for quenching of the singlet excited state by an external quencher (carbon tetrachloride) (Q) and τ_0 is the lifetime of the singlet excited state in the absence of Q. This rate constant is then inserted into eq 3,[17] in which Λ_s is the singlet energy

$$\Lambda_s/D = (k_q{}^{\text{polymer}} - (1/2)k_q{}^{\text{monomer}})/(1/2)k_q{}^{\text{monomer}} \qquad (3)$$

migration rate, D is the diffusion constant of the quencher (Q), and k_q are the quenching rates for the polymer and monomer determined from the Stern−Volmer treatment. In the derivation of eq 3, it was assumed that $\Lambda_s = 0$ for the monomer and that diffusion between segments of polymer is negligible.[17] Thus, nonzero values of Λ_s/D establish only the operation of energy migration, but of no quantitative rate. Ratios of Λ_s/D greater than unity reflect directional energy migration over an excitation diffusion distance Λ_s (based on a one-dimensional random walk).[21] Λ_s is then obtained by inserting the appropriate values into eq 4, where τ_0 is the intrinsic lifetime of the singlet excited state.

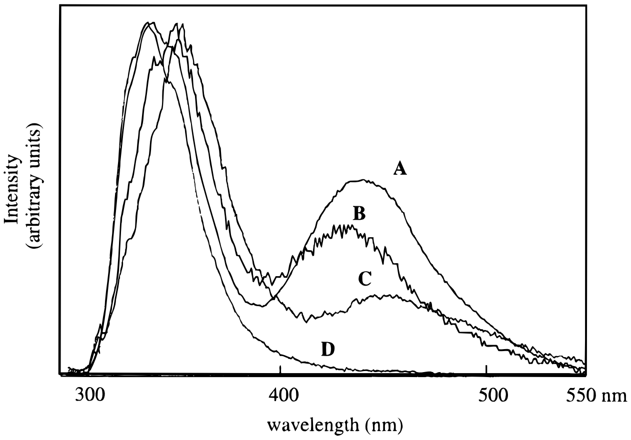

Figure 3. Fluorescence spectra of **IIIa** (10^{-5} M) in (A) CH_2Cl_2, (B) THF, (C) THF/CH_3CN (2:1), and (D) $CHCl_3$; $\lambda_{ex} = 284$ nm.

$$L_s = (2L_s\tau_0)^{1/2} \qquad (4)$$

Table 2 lists values of Λ_s/D greater than unity for **IIa** and **IIb,** indicating that energy migration in these two polymers is significant and spans relatively large distances (56 and 97 Å, respectively). For **IIc,** Λ_s/D is less than 1: as a consequence, energy migration is relatively inefficient, progressing over only about 18 Å before decay.

B. Solvent Effects on Emission and Ion Pair Formation in Copolymers III. An important perturbation of observable polymer photophysics is the influence of solvent. It is well established that polar solvents stabilize polar intermediates, especially for D−A ion pairs whose stabilities are governed by the energy gap law and whose energetics lie in the Marcus inverted region (for exciplexes with large charge separation).[16] More specifically, polar solvents have the potential to partially solvate, or even completely dissociate, exciplexes. Since we ultimately wish to produce solvent-separated ion pairs with positive and negative charges physically separated by long distances, we have examined the effect of increasing solvent polarity on the excited-state properties of **IIIa**−**d.** The fluorescence spectra of **IIIa**−**d** in a series of solvents are overlaid in Figures 3−6. (A mixed solvent THF/CH_3CN was employed because of the limited solubility of the polymers.) The intensities of the long-wavelength emissions (at 450−500 nm) assigned to exciplex decrease as the solvent polarity is increased, Table 3. Because THF ($P' = 4.0$) is more polar than CH_2Cl_2 ($P' = 3.1$),[23] the fraction of the observed total emission attributable to exciplex in THF decreases by 17%, 3%, and 15% respectively for **IIIa**, **IIIb**, and **IIId** from that observed in CH_2Cl_2. By mixing THF with CH_3CN ($P' = 5.8$) in a 1:1 ratio, the exciplex emission intensity decreased even further (by 38%, 19%, and 45%, respectively). Further attempts to suppress exciplex emission by adding larger quantities of CH_3CN resulted only

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(23) Snyder, L. R. *Principles of Adsorption Chromatography*; Marcel Dekker, Inc.: New York, 1968. (Note: P' is defined as a relative measure of the degree of interaction of the solvent with various polar test solutes. P' increases with increasing solvent polarity.)

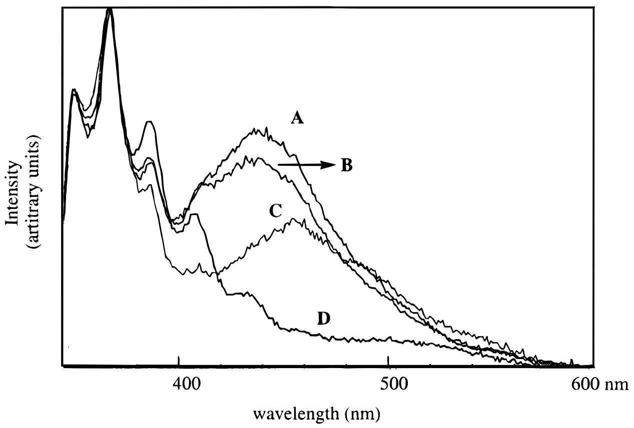

Figure 4. Fluorescence spectra of **IIIb** (10^{-5} M) in (A) CH_2Cl_2, (B) THF, (C) THF/CH_3CN (2:1), and (D) $CHCl_3$; λ_{ex} = 335 nm.

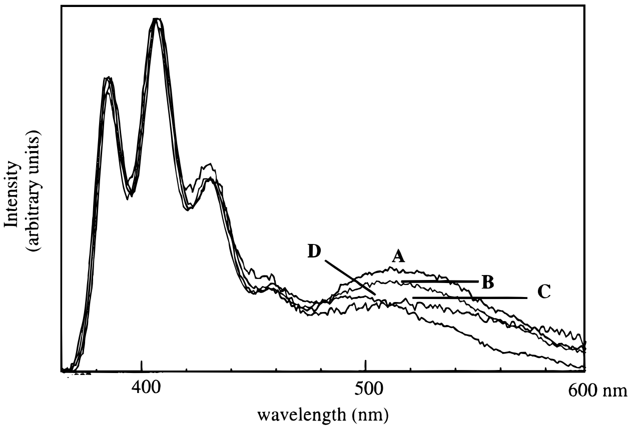

Figure 5. Fluorescence spectra of **IIIc** (10^{-5} M) in (A) CH_2Cl_2, (B) THF, (C) THF/CH_3CN (2:1), and (D) $CHCl_3$; λ_{ex} = 355 nm.

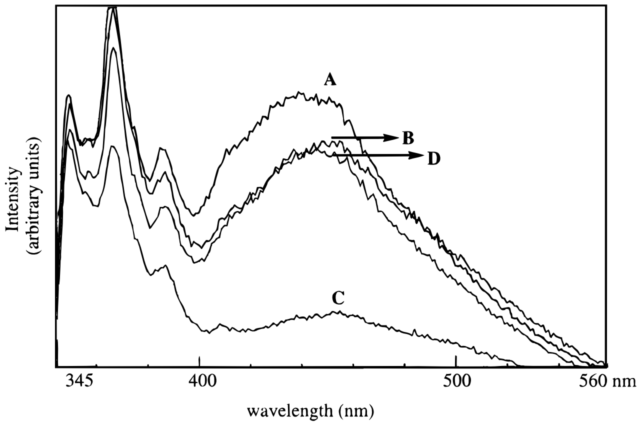

Figure 6. Fluorescence spectra of **IIId** (10^{-5} M) in (A) CH_2Cl_2, (B) THF, (C) THF/CH_3CN (2:1), and (D) $CHCl_3$; λ_{ex} = 355 nm.

in precipitation of the polymer. Such insolubility is inevitable because of the incompatibility of the nonpolar polymer backbone with very polar solvents.

Whether the suppression of exciplex emission could be correlated with ion pair formation was probed by transient absorption measurements. Transient absorption of the radical ion pair produced by flash excitation of these block copolymers **III** in THF was sought by monitoring at the following wavelengths: **IIIa** at that for the naphthalene radical anion (755−840 nm); **IIIb,d** at that for the phenanthrene radical anion (450 and 850 nm); **IIIc** at the wavelength reported for the anthracene radical anion (650−800 nm); **IIIa**−**c** at that for the dimethylaniline radical cation (475 nm); and **IIId** at that for the dicyanobenzene radical anion (344 nm).[24] However, such studies yielded no evidence for production of the charge-separated ions in the block copolymers **III**. Presumably, either the low-energy exciplex in **III** acts as a trap, inhibiting photoinduced charge separation, or rapid back electron transfer at a single interface quenches potential ion pair formation. The polar solvents apparently provide a pathway for exciplex relaxation without stabilizing the interface-confined radical ions on the nanosecond time scale.

Table 3. Solvent Effects on the Relative Integrated Intensities of Exciplex Emission[a,b] in Copolymers **IIIa**−**c**

diblock copolymer	CH_2Cl_2	THF	THF/CH_3CN (1:1)	$CHCl_3$
IIIa	1.0	0.83	0.62	0.00
IIIb	1.0	0.97	0.81	0.10
IIIc	1.0	0.85	0.55	0.15
IIId	1.0	0.97	0.55	0.93

[a] Normalized to the intensity observed in CH_2Cl_2. [b] Emission measured in THF as a 10^{-5} M solution.

A dramatic change in the emission spectra of **IIIa** and **IIIb** is observed in $CHCl_3$ (P' = 4.1), where complete quenching of the exciplex emission of **IIIa** and a 90% quenching in **IIIb**, along with a significant decrease in monomer emission, are observed.[25] In contrast to **IIIa** and **IIIb**, **IIId** shows only minimal quenching of the exciplex (similar to the situation observed in THF) in $CHCl_3$. The most obvious differences in copolymers **III** are the size and excited-state lifetimes of the pendent chromophores. In addition, solvent interactions which suppress the exciplex emission in **IIIa** and **IIIb** (bearing the dimethylanilino donor) differ in character from those copolymers bearing the dicyanophenyl acceptor (**IIId**). It is possible, for example, that in $CHCl_3$ the $DMA^{\bullet+}$/$arene^{\bullet-}$ exciplex transfers an electron to the solvent, thereby quenching the exciplex emission, whereas the $arene^{\bullet+}$/$DCP^{\bullet-}$ exciplex does not. We attempted to test this hypothesis by measuring the emission of these polymers in a solvent more easily reduced than $CHCl_3$ (i.e., CCl_4). However, the polymers are not sufficiently soluble to permit observation of solution-phase fluorescence.

Time-resolved emission measurements of **IIIa** and **IIIb** in $CHCl_3$ reveal a decreased singlet-excited-state lifetime (by approximately 50%) compared with that in THF. Transient absorption of **IIIb** in $CHCl_3$ shows a signal growing in at 450 nm (assigned to the phenanthrene radical cation) as a shoulder on the phenanthrene triplet emission (460−510 nm). Unfortunately, the transient absorptions of the phenanthrene radial anion, radical cation, and triplet overlap strongly, so that separate signals could not be adequately resolved. The same measurements in **IIIa** were attempted upon excitation at 266 nm. However, absorption by the dimethylanilino groups competes effectively with absorption by the naphthyl groups at this wavelength, and a complex excitation profile resulted.

Transient absorption of **IIIc** showed no unambiguous sign of separated radical ions in either chloroform or THF.[26] In contrast to the solvent effects on **IIIa**, **IIIb**, and **IIId**, the intensity of exciplex emission in **IIIc** changes only minimally

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[24] Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: New York, 1988; pp 264−300.

[25] We have eliminated adventitious acid in $CHCl_3$ as a source of the decrease in exciplex emission by shaking the solvent with solid potassium carbonate prior to each use. Unfortunately, $CHCl_3$ is not a suitable solvent for transient measurements, because of its high reactivity with light to form acidic species in solution.

[26] Extended laser pulsing (30 min) of **II**−**IV** resulted in degradation of the polymers as characterized by fluorescence spectra before and after extended laser excitation.

[27] Scaiano, J. C. *CRC Handbook of Organic Photochemistry*; CRC Press, Inc.: Boca Raton, FL, 1989; pp 376−389.

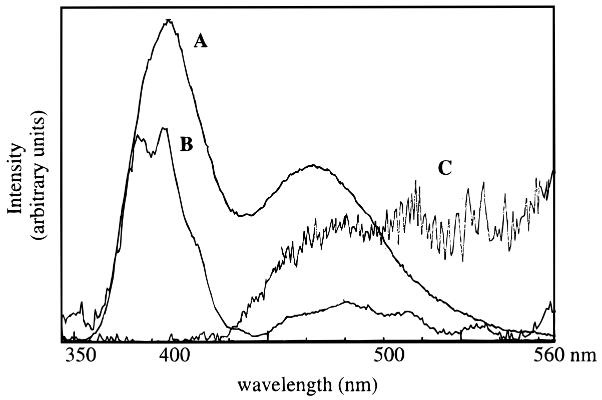

Figure 7. Fluorescence and phosphorescence spectra of **IIIa** (10^{-5} M) in MTHF, $\lambda_{ex} = 284$ nm: (A) fluorescence at room temperature; (B) total emission at 77 K; (C) phosphorescence (using a chopper) at 77 K.

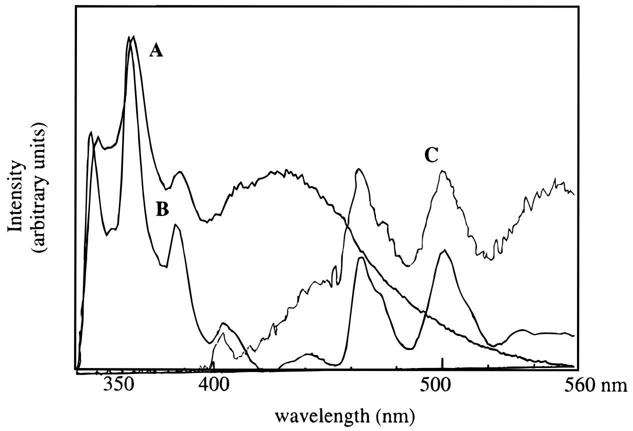

Figure 8. Fluorescence and phosphorescence spectra of **IIIb** (10^{-5} M) in MTHF, $\lambda_{ex} = 335$ nm: (A) fluorescence at room temperature; (B) total emission at 77 K; (C) phosphorescence (using a chopper) at 77 K.

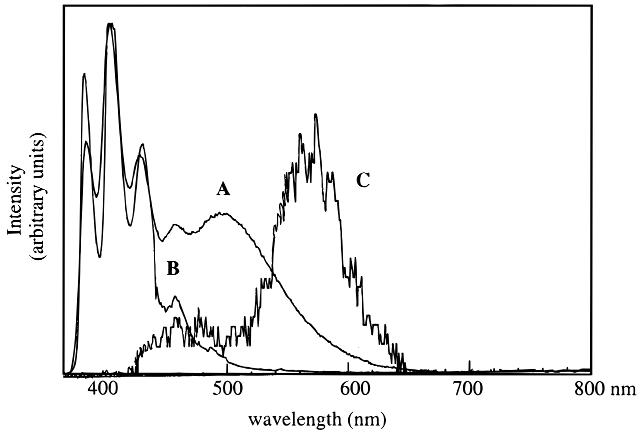

Figure 9. Fluorescence and phosphorescence spectra of **IIIc** (10^{-5} M) in MTHF, $\lambda_{ex} = 355$ nm: (A) fluorescence at room temperature; (B) total emission at 77 K; (C) phosphorescence (using a chopper) at 77 K.

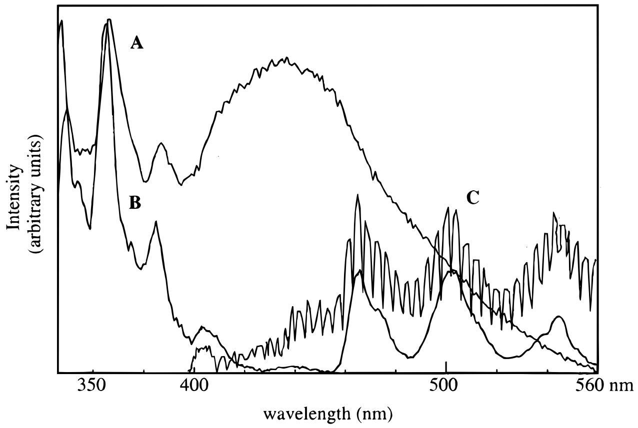

Figure 10. Fluorescence and phosphorescence spectra of **IIId** (10^{-5} M) in MTHF, $\lambda_{ex} = 355$ nm: (A) fluorescence at room temperature; (B) total emission at 77 K; (C) phosphorescence (using a chopper) at 77 K.

with solvent. Thus, the energetics for solvation must be much lower in **IIIc** than in **IIIa**, **IIIb**, or **IIId**.

The component chromophore−quencher interactions of **IIIa−d** were modeled by studying an intermolecular analog of these interactions by employing the related monomers in this same series of solvents. The calculations described above have shown that the energy migration rates are slower than diffusion (about 10^{10} s^{-1}) of a dissolved quencher. Smaller chromophores allow better solvation of the chromophore−quencher pair than larger ones, and enhanced quenching is thus expected. With 10^{-5} M solutions of naphthalene, phenanthrene, or anthracene in CH_2Cl_2, THF, and THF/CH_3CN (1:1), exciplex emission is observed upon adding 35−55 mL of dimethylaniline. In $CHCl_3$, however, exciplex emission is completely suppressed for both naphthalene and phenanthrene, but virtually no decrease is observed with anthracene. In 10^{-5} M solutions of phenanthrene in CH_2Cl_2, THF, THF/CH_3CN (1:1), or $CHCl_3$, exciplex emission is still observed upon adding a 50 mM solution of dicyanobenzene. These results confirm the expectation that chromophore size and excited-state characteristics do indeed influence a group's ability to form exciplex with donors or acceptors both as low molecular weight bimolecular pairs and as intramolecular pairs produced at the block interface of our polymers. These bimolecular experiments also rationalize our observation that dicyanobenzene-labeled block copolymers (**IIId**) display quite different solvent effects than those bearing dimethylanilino groups (**IIIa−c**). The varying effect of chloroform likely depends on the redox properties of the appended chromophore.

C. Temperature Effects on Emission from Block Copolymers III. The excited-state properties of polymers are significantly affected by their equilibrated conformations in solution. Therefore, in order to segregate electronic effects from those that result from the dynamic motion of the polymers during the measurement, we have investigated the emission (fluorescence and phosphorescence) of block copolymers **III** in a MTHF glass at 77 K. The emission spectra observed for **IIIa−d** are presented in Figures 7−10, in which are overlaid a fluorescence spectrum measured at room temperature (curves A), a composite fluorescence and phosphorescence emission spectrum measured at 77 K (curves B), and a phosphorescence emission spectrum[28] measured at 77 K with the use of a chopper to eliminate prompt emission (curves C). Exciplex emission was suppressed in the spectra of any of the block copolymers **III** at 77 K (curves B), in contrast to the strong emission observed at room temperature (curves A). The exciplex emission observed at room temperature must therefore be frozen out by an insurmountable energy barrier at low temperature, by suppression of solvent reorganization, or by prevention of the formation of the exciplex at 77 K because of restricted molecular motion.

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[28] The phosphorescence spectra (curves C) were similar to those previously reported for the phosphorescence of low-temperature solutions of the parent chromophore. (a) Naphthalene: Takemura, T.; Baba, H.; Shindo, Y. *Chem. Lett.* **1974**, 1091−1096. (b) Anthracene: Itoh, Y.; Webber, S. E. *Macromolecules* **1990**, *23*, 5065−5070. (c) Phenanthrene: Parker, C. A.; Hatchard, C. G. *Analyst* **1962**, *87*, 664−676.

Table 4. Excited-State Lifetimes of the Emitting State of Phenanthryl-Containing Block Copolymers **IIId**, **IIIb**, **IVa**, **IVb**, and **IVd**[a]

	monomer (λ_{em} = 375 nm)		exciplex (λ_{em} = 460 nm)	
	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)
IIIb	7.6 (±0.16)	20 (±0.02)	8.3 (±0.02)	27 (±0.13)
IIId	0.99 (±0.01)	14 (±0.06)	1.5 (±0.04)	6.4 (±0.05)
IVa	0.99 (±0.05)	15 (±0.13)	1.6 (±0.04)	8.0 (±0.22)
IVb	0.98 (±0.01)	6.5 (±0.04)	1.2 (±0.02)	6.5 (±0.06)
IVd	0.99 (±0.04)	4.1 (±0.06)	1.1 (±0.02)	9.7 (±0.12)

[a] Emission measured at 355 nm in THF as $10^{-5}-10^{-4}$ M degassed solutions.

In **IIIa**, **IIIb**, and **IIId**, shown in Figures 7, 8, and 10, we observe both fluorescence *and* phosphorescence at 77 K, without the chopper in place. In contrast, under these conditions **IIIc** shows no visible phosphorescence, Figure 9B, but with the chopper in place and the intensity normalized, we can observe phosphorescence (Figure 9C). The low intensity of phosphorescence in **IIIc** is probably caused by the low quantum yield for intersystem crossing (singlet to triplet) in anthracene (F_{ST} = 0.0003), compared to that for naphthalene (F_{ST} = 0.40) or phenanthrene (F_{ST} = 0.16).[27]

Transient absorption spectra of **IIIa**–**d** at 77 K in MTHF again show no clear evidence for long-lived charge-separated radical ions, although in **IIIb** long-lived phosphorescence could be observed for seconds after excitation.

D. Steady-State and Transient Emission from Block Copolymers of (Dimethylanilino)$_x$–(Phenanthryl)$_y$–(Dicyanophenyl)$_z$ IV with Varying Phenanthrene Block Length. The key structural components of **IIIb** and **IIId** were combined in **IVa**–**d** to search for observable photoinduced charge separation. In polymers **IV**, the attached groups are ordered according to the redox potentials of DMA (E_{ox} = +0.85 V), phenanthrene (E_{ox} = +1.60 V, E_{red} = −2.0 V), and DCB (E_{red} = −1.64 V) so that these pendent groups are placed sequentially along the backbone to create a redox gradient for vectorial electron transfer. The excited states of polymers **IVa**–**d** were examined by transient emission and steady-state spectroscopy and were compared to the corresponding copolymers **IIIb** and **IIId**. The individual members of the series **IV** differed by the length of the intervening phenanthryl relay block.

1. Transient Analysis. The lifetimes of the excited states of the pendent groups present in block copolymers **IIIb** and **IIId** were compared with those in block copolymers **IVa**–**d** upon excitation at 355 nm, with emission being monitored at 375 nm and 460 nm, Table 4. Biexponential decay is observed both with the isolated (monomer) chromophores and with the exciplex. The emission spectra of **IIIb** and **IIId** show biexponential decay at both 375 and 460 nm. These biexponential decays are assigned to two different interconverting excited-state species present in the copolymers (monomer and exciplex). At 460 nm, the emission decay for **IVb** also shows a rise (measurable energy migration), while **IIId** does not (an energy migration rate too fast to measure on a nanosecond time scale), *vide supra*. Similar spectral features are observed in **IVa**–**d**.

Next, we systematically varied the block length of the phenanthryl relay block to investigate the effect of the absorber block length on the efficiency of energy and/or electron transfer. In block copolymers **IVa**, **IVb**, and **IVd** with short phenanthryl block lengths, the long-lifetime component of the phenanthryl (monomer) emitter decreases with block size, implying that quenching is increased by rapid random migration of the exciton to one of the two quencher blocks on either side of the phenanthrene: namely, by interaction at the dimethylaniline (donor) and dicyanobenzene (acceptor) interfaces. The observed exciplex emission lifetimes in **IVa**, **IVb**, and **IVd** are much less affected by block size but also decreases in parallel with the monomer emission. The emissions of copolymers **IVa**–**d** do not show a resolvable rise time for the formation of exciplex, probably because of fast energy migration, as surmised earlier for **IIId**.

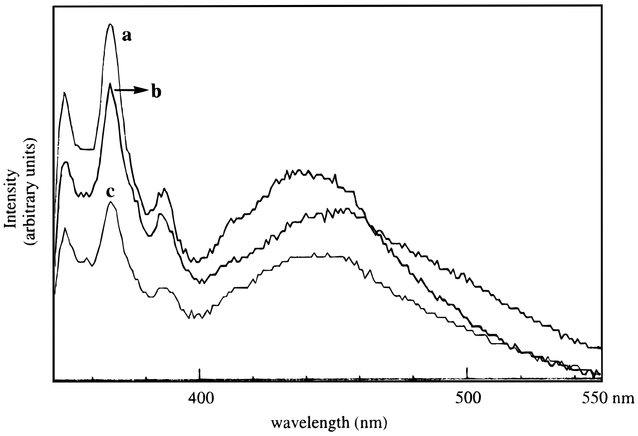

Figure 11. Steady-state fluorescence of (a) **IIIb**, (b) **IIId**, and (c) **IVa** (10^{-5} M) in CH_2Cl_2 at an optical density of 0.1 AU.

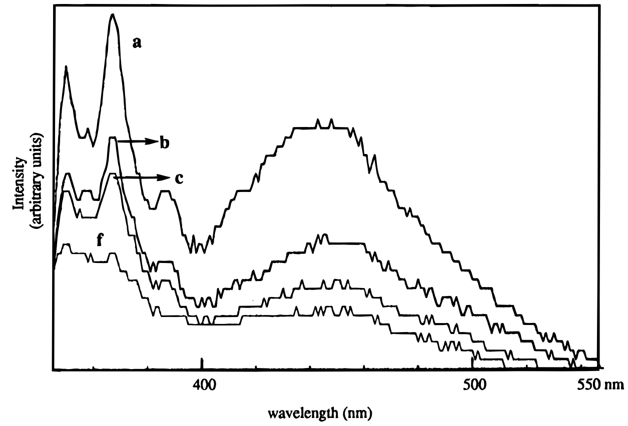

Figure 12. Steady-state fluorescence emission of (a) **IVa**, (b) **IVb**, (c) **IVc**, and (d) **IVd** (10^{-5} M) in CH_2Cl_2 at an optical density of 0.1 AU.

E. Steady-State Analysis. Next, the steady-state fluorescence spectra of copolymers **IIIb, IIId, IVa, IVb,** and **IVd** were analyzed to obtain information about their relative emission intensities. A comparison of the fluorescence spectra of **IIIb** and **IIId** with that of **IVa** is shown in Figure 11. The short-wavelength emission at 375 nm, assigned to the phenanthryl group, decreases as the number of excited-state quenchers increases from one in **IIIb** or **IIId** to two in **IVa**. Here, the intensity of the long-wavelength emission at 450 nm, assigned to exciplex, is increased slightly by the presence of the two quenchers in **IVa** from that observed in **IIIb** or **IIId**.

The fluorescence spectra of blocks **IVa**–**d** are shown in Figure 12. In Figure 12A, the intensity of the emission at 375 nm, assigned to an isolated phenanthryl singlet excited state, decreases with the length of the phenanthryl block from **IVa** to **IVd**. The exciplex emission at 450 nm also decreases slightly in intensity as the phenanthryl block length decreases from **IVa** to **IVd.**

A summary of the observed emission intensities in **III** and **IV** is presented in Table 5. The efficiency of quenching of the phenanthryl monomer emission in **IV** is much higher than that in the corresponding homopolymer **IIb**, with increased quenching being observed with shorter phenanthrene-block size where

Table 5. Fluorescence Emission[a] of a Series of Phenanthrene Copolymers **IV** Compared with Copolymers **IIIb** and **IIId**

copolymer	quenching efficiency of monomer emission rel to **IIb**, %	quenching efficiency of exciplex emission rel to **IIIb**, %
IIIb	64	0
IIId	60	0
IVa	75	11
IVb	84	20
IVc	83	19
IVd	93	29

[a] Column 2 represents the fractional quenching of the monomer emission in the block copolymers compared with that observed in homopolymer **IIb**. Column 3 represents the percent quenching of the exciplex emission in **IV** compared with that in **IIIb**. Spectra were measured in degassed THF as 10^{-5} M solutions at room temperature.

the migration to a quenching interface requires fewer hops.[29] The intensity of monomer emission in **IIIb** is only slightly lower than that observed in **IIId**, whereas in **IVa** this emission is noticeably lower by another 15%. This behavior indicates that the phenanthrene excited-state energy can statistically migrate to either the dimethylanilino donor or the dicyanophenyl acceptor to quench the observed fluorescence. Conversely, if we compare the relative intensities of exciplex emission in the normalized spectra, the emission in **IVa** is quenched by only 10% more in **III**, i.e., not double as might be expected with two quenchers on either side of the chromophore block.

By comparison with **IIId**, the relative intensities of monomer emission in **IVb**, **IVc**, and **IVd** are quenched by an additional 24%, 23%, and 33%, respectively.[29] Thus, the presence of a second quencher suppresses monomer emission. Moreover, this monomer quenching is not accomplished by enhanced exciplex emission, for a comparison of the exciplex emission in **IIIb** and **IIId** with that observed in **IV** indicates that the amount of exciplex emission is actually lower in **IVb**, **IVc**, and **IVd** (with higher levels of monomer quenching) than in **IVa** (with the lowest level of monomer quenching).

There are two plausible explanations for the observed decrease (rather than an expected increase) in the intensity of exciplex emission of **IV** over that in **IIIb**: (1) preferential migration of the phenanthryl excitation energy to the DCB quencher on one side of the block may dominate over energy migration to the DMA quencher on the other side; or (2) energy migration to the quenchers on either block interface in **IV** results in photoinduced electron transfer rather than exciplex emission. The first possibility is unlikely because comparable driving forces are involved in the energy migration to either interface. Rather, when the components of copolymers **IIIb** and **IIId** are combined in **IV**, random walk theory predicts that energy will migrate nonselectively via the shortest path to the nearest electron transfer trap.[21] It is likely therefore that the decreased exciplex emission is caused by enhanced electron transfer at the two interfaces present in **IV**.

F. Transient Absorption and Photoinduced Charge Separation in Triblock Copolymers IV. To test the latter explanation, we performed transient absorption measurements on **IV** to seek evidence for the proposed photoinduced electron transfer, i.e., for the production of a physically separated radical ion pair. Using nanosecond flash excitation techniques, we obtained direct evidence for photoinduced electron transfer resulting in the formation of charge-separated dicyanobenzene ($DCB^{\bullet-}$) and dimethylaniline ($DMA^{\bullet+}$) radical ion pairs in **IVa**–**d**. Transient absorption of **IVa** shows not only absorption from the phenanthrene triplet but also an absorption at 344 nm (typical for the transient absorbance of $DCB^{\bullet-}$)[24] and indirect evidence for the $DMA^{\bullet+}$ (typical transient absorbance at 475 nm)[24] barely resolvable from the triplet, Figure 13C. The existence of this latter band can be seen more clearly upon comparing the excited-state spectrum of **IVa** (Figure 13C) with those of **IIIb** and **IIId**, Figure 13, parts A and B, respectively. Since **IIIb** and **IIId** only show absorption from the phenanthrene triplet, the difference in the curve shape of the transient in Figure 13C plainly shows the existence of an additional peak at around 470–480 nm. Attempts to selectively quench the triplet by bubbling oxygen through the solution prior to laser excitation resulted in significant quenching of all signals, not only the triplet.

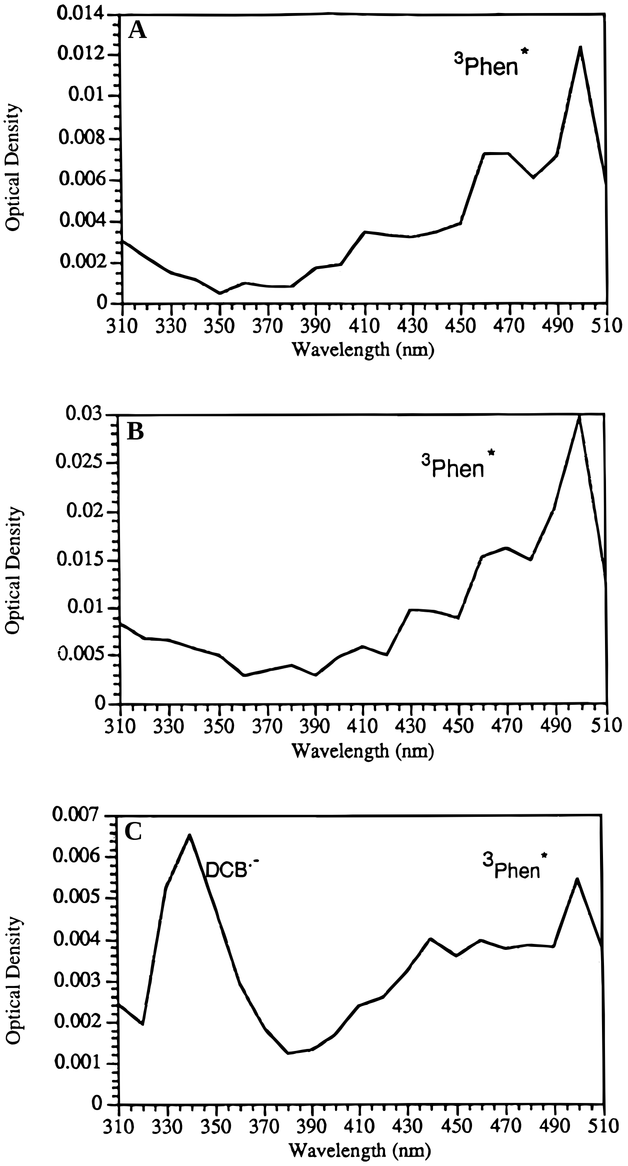

Figure 13. Transient absorption spectra on a 10-μs time scale in THF. (A) **IIId**: phenanthrene triplet (400–500 nm). (B) **IIIb**: phenanthrene triplet (400–500 nm). (C) **IVa**: $DCB^{\bullet-}$ (344 nm), $DMA^{\bullet+}$ (475 nm), and phenanthrene triplet (400–500 nm).

The possibility of intermolecular electron transfer in **IV** under our experimental conditions has been ruled out by both

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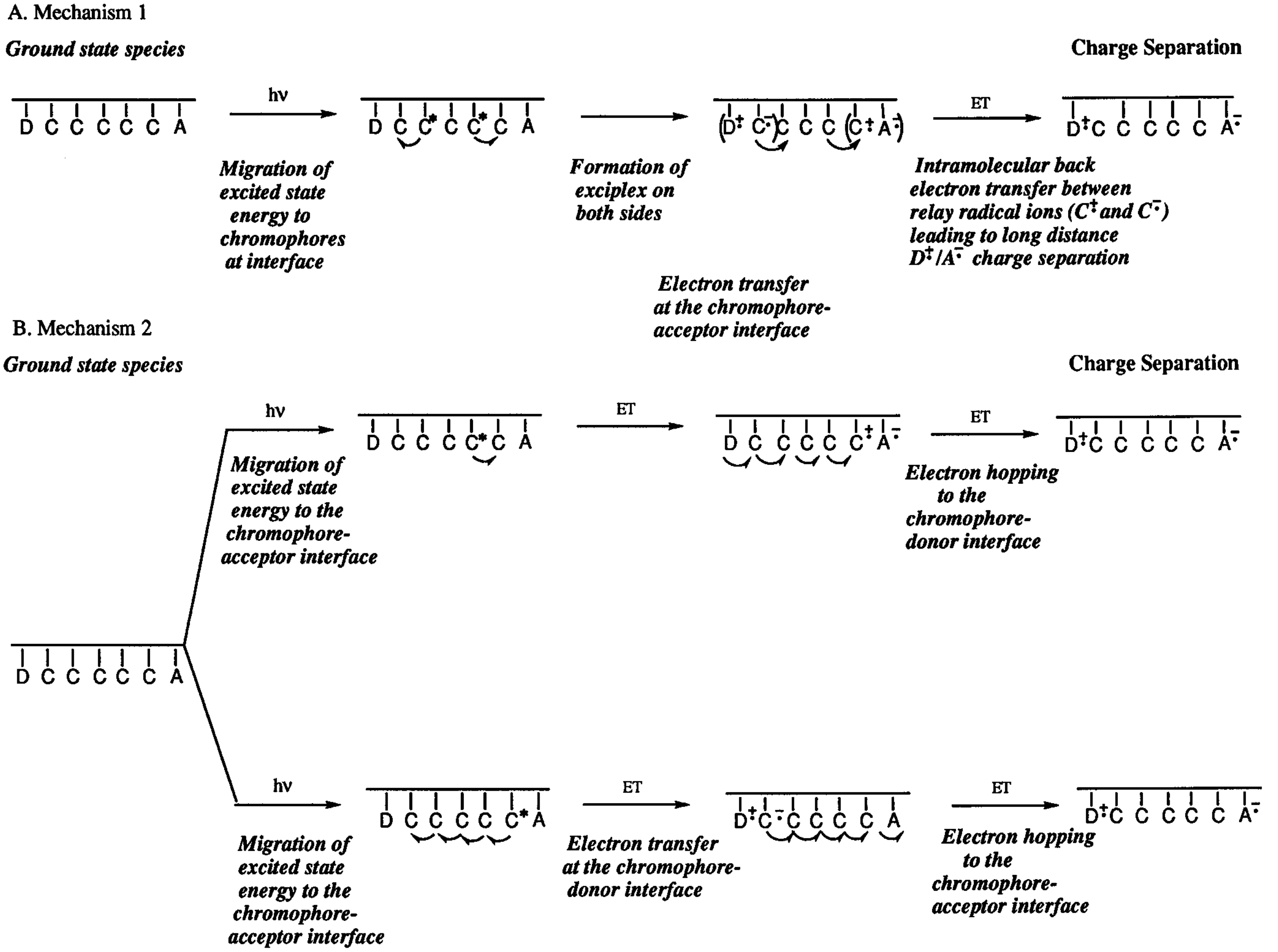
(29) Odian, G. *Principles of Polymerization*; Wiley: New York, NY, 1992. The similarity in quenching in **IVb** and **IVc** may stem from the fact that the block copolymers containing fewer than five phenanthrene units between the donor and acceptor may not be truly monodisperse. The statistical nature of chain growth in living polymerizations dictates that the rates of initiation and propagation vary greatly for small block sizes, making it difficult to add only one to two units at a time. The result is usually larger polydispersity indices for polymers containing small block lengths.

(30) Chatterjee, P. K.; Kamioka, K.; Batteas, J. D.; Webber, S. E. *J. Phys. Chem.* **1991**, *95*, 960–965.

Scheme 1. Two Possible Mechanisms Leading to Long-Range Charge Separation on a Single Polymer Chain Bearing a Donor (D), Acceptor (A), and Relay/Chromophore (C) on a Rigid Polymer Chain[a]



[a] Mechanism 1: a biphotonic process involving energy migration and electron transfer. Mechanism 2: a single-photon process involving energy migration and electron transfer.

experiment and calculation. The concentration of polymer in the transient experiments is 1.5 × 10^{-5} M. Assuming an upper limit for the intermolecular diffusion rate of 10^{10} s^{-1} M^{-1}, we calculate an intermolecular interaction to occur every 6 × 10^{-6} s (6 μs). Since the lifetime of the phenanthrene chromophore is only 16 ns, full relaxation would therefore have taken place long before any intermolecular interactions could occur. Hence, we rule out intermolecular interactions as a significant source of radical ion formation. Furthermore, by experimentation, transient absorption experiments combining **IIIb** and **IIId** at the same phenanthrene concentration as in **IV** showed no signs of a DCB radical anion at 344 nm. The contrasting behavior in **IV** implies that the charge separation observed in **IV** cannot occur intermolecularly and, instead, depends on intramolecular energy migration followed by charge trapping at both interfaces.

The absorption decay curve assigned to $DCB^{\bullet-}$ at 344 nm in **IVa**, Figure 14, can be fitted to a single exponential with a lifetime of 7.2 ± 0.04 μs. The transients assigned to $DCB^{\bullet-}$ in **IVb** and **IVc** have lifetimes of 6.0 ± 0.05 and 5.7 ± 0.1 μs, respectively. These lower lifetimes in **IVb** and **IVc** than in **IVa** correlate directly with the shorter phenanthrene block lengths separating the oxidized DMA cation from the reduced DCB anion in the former compounds. This observation suggests stronger electronic coupling and/or more rapid back electron transfer in block copolymers bearing ion pairs separated by smaller intervening relay distances.

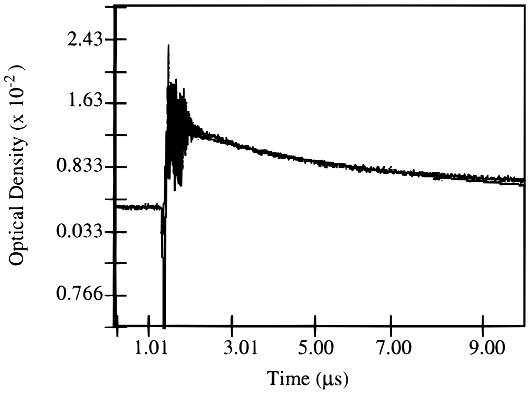


Figure 14. Transient absorption decay curve of **IVa**: DCB radical anion at 344 nm, OD = 0.25 AU at λ_{ex} = 355 nm. Single exponential fit with lifetime of 7.2 μs.

Two possible modes of photoinduced electron transfer in **IV** are shown in Scheme 1. In the first mechanism, excitation of two ground-state phenanthryl pendent groups (questionably assuming a biphotonic absorption at 30 mJ/pulse) results in simultaneous energy migration to the donor and acceptor blocks at either end, where oxidation and reduction take place. The radical anion and cation of phenanthrene later recombine, stranding a charge-separated DCB radical anion and a DMA radical cation at opposite sides of the relay block. In the second mechanism, following excitation of a single phenanthryl group and energy migration to the donor or acceptor at either end, electron transfer takes place to form a phenanthrene radical anion (or radical cation) and a DMA radical cation (or DCB radical anion). The extra electron then hops through the phenanthrene block to the other interface, ultimately producing the counterion. As the length of the phenanthryl block separating the donor and acceptor increases, the distance between the radical ions becomes greater and, hence, their transient lifetimes become longer,[31] but the probability of their formation becomes lower because random migration competes less successfully against natural excited-state relaxation. By either mechanism, these radical ions ultimately recombine (by back electron hopping) to regenerate the ground state.

The important observation of this experiment is that, in our carefully designed copolymers **IV**, photoinduced charge separation has been sustained for microseconds. The next goal in this research program is to extend the lifetime of the charge separation by increasing the phenanthryl block length separating the donor and acceptor without too adversely interfering with excitation migration efficiency to the two block interfaces.[31]

Conclusions

Block copolymers **IIIa−c** show rather slow energy migration between pendent aromatic groups, as shown by the rise times observed in their transient emission spectra. Solvent polarity has a significant effect on the efficiency of exciplex emission in **IIIa** and **IIIb**, simultaneously stabilizing the polar exciplex and quenching its emission by 50%. Low-temperature spectra of **IIIa−c** show nearly complete quenching of exciplex emission, possibly because of conformational rigidity of the chromophore and quencher at the interface, inhibited solvent reorganization, or restricted molecular motion. Steady-state and transient emission spectra of the block copolymers **IVa−d** show decreased monomer emission and lifetimes upon decreasing the length of the intervening phenanthryl block. This observation is consistent with directional charge separation in **IV**. Transient absorption spectra indicate that successful charge separation in **IV** produces an ion pair whose lifetime is dependent on the distance separating the donor and the acceptor blocks on either side.

Acknowledgment. We are grateful to the Office of Basic Energy Sciences, U.S. Department of Energy, for support of this work. We thank Thomas Martin for assistance with fitting rise times in the transient emission experiments. We are grateful to Dr. Donald O'Connor at the Center for Fast Kinetics Research for helpful discussions and for assistance with the single photon counting and transient absorption measurements. Special thanks to Renae Fossum for her time and assistance with several control experiments reported in the final version of this manuscript.[31]

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(31) We have prepared two more members of series of **IV** with longer phenanthrene spacers and have observed larger differences and longer lifetimes in the radical species formed (i.e., dcb$_5$-phen$_{20}$-dma$_5$, τ (DCB$^{\bullet -}$) = 26 ms, and dcb$_5$−phen$_{40}$−dma$_5$, τ (DCB$^{\bullet -}$) = 32 ms). We do not expect an exponential drop-off of lifetime with distance, since these systems go through multiple electron and energy transfers in order to achieve charge separation. Therefore, the rate of back electron transfer drops off to 3% over a distance of 7 Å (assuming a typical β value) once the electron moves by one chromophore away from the interface. Hence, with a longer relay block length between the donor and the acceptor block, charge recombination has a lower probability and, hence, longer-lived charge separation.