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Rigid, Well-Defined Block Copolymers for Efficient Light Harvesting

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Chromophore-labeled polymers have been studied extensively for their potential application in long-distance energy and electron transfer.[1-6] The conformational flexibility of most organic polymers, however, has prevented the successful transfer of energy over extended distances because polymer folding permits energy dissipative excimer or exciplex formation.[1-3,5] In addition, the limited number of methods[6,7] available to prepare well-defined photosensitizer-derivatized block copolymers has hindered the use of polymers as media for macroscopic photoinduced electron transfer. We report the synthesis and photophysical characteristics of a series of well-defined chromophore- and quencher-labeled block copolymers whose rigidity obviates these problems and permits interblock energy and electron transfer.

For some time we have been interested in preparing polymer-based systems capable of efficient light collection, long-range photoinduced electron transfer, and ultimately, long-lived charge separation.[5] To accomplish this task we have used ring-opening metathesis polymerization[6,7] to form monodisperse polymers and/or organized block copolymers (typical polydispersity = 1.2–1.3) of known spacing and stoichiometry.[8] Selection of an appropriate series of photosensitizers and quenchers placed sequentially along the rigid polymer backbone allows for vectorial energy migration and/or photoinduced electron transfer, ultimately producing one-dimensional charge separation along the polymer chain by the sequence of photophysical steps illustrated in Figure 1. We have prepared arene-derivatized polynorbornene homopolymers I, arene–dimethylaniline diblock copolymers II, and naphthalene–pentamethylbenzene–dimethylaniline triblock copolymers, III, of varying molecular weights and block lengths.

Steady-state fluorescence studies demonstrate the rigidity of these photosensitizer-labeled polymers. First, the steady-state emission spectrum of the naphthalene-derivatized homopolymer Ia in dichloromethane (λ_{max} = 335 nm, Figure 2) is virtually identical to that of a dilute solution of naphthalene and shows no sign of the red-shifted excimer emission that has been reported as a broad band at ~400 nm.[1b] Second, exciplex emission is not observed in the steady-state fluorescence spectrum of the triblock copolymer III: instead, a fluorescence spectrum identical to that in Figure 2 is observed. This result is a clear indication that

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(6) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907.
(7) (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158. (b) Albagli, D.; Bazan, G.; Wrighton, M. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 7328.
(8) The block copolymers were prepared by the technique described by Schrock.[7] Monomer synthesis and polymer purification and characterization are described in the supplementary material. [1]H and ^{13}C nuclear magnetic resonance spectra indicate polymer regularity, with 88% *trans* stereochemistry at the olefin linkages. Gel permeation chromatography, calibrated against polystyrene, and end group analysis showed low polydispersity: Ia, M_n = 45 761 (M_w/M_n = 1.2); Ib, M_n = 11 430 (M_w/M_n = 1.2); IIa, M_n = 9139 (M_w/M_n = 1.3); IIb, M_n = 9366 (M_w/M_n = 1.2); III, M_n = 12 000 (M_w/M_n = 1.4).
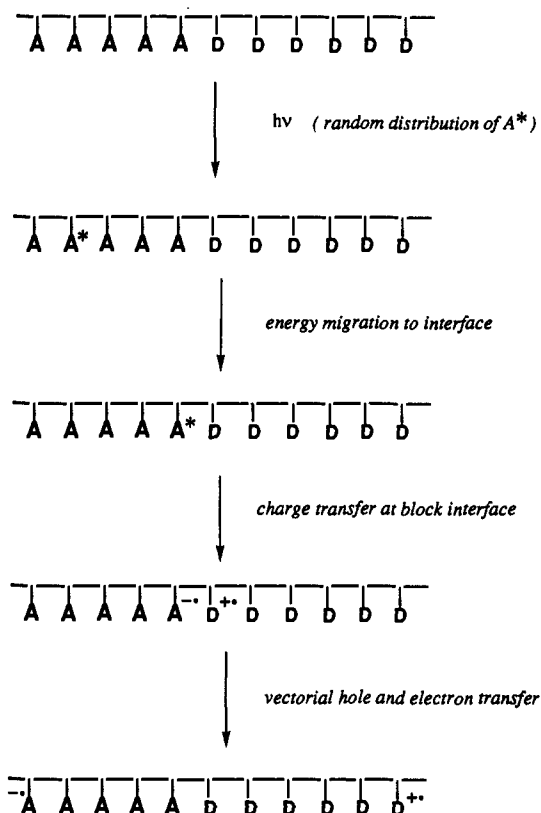

Figure 1. Schematic representation of long-range charge separation by photoinduced energy migration and electron transfer on a chromophore-quencher-labeled rigid block copolymer in which the excited chromophore A acts as an electron acceptor and the quencher D acts as an electron donor.
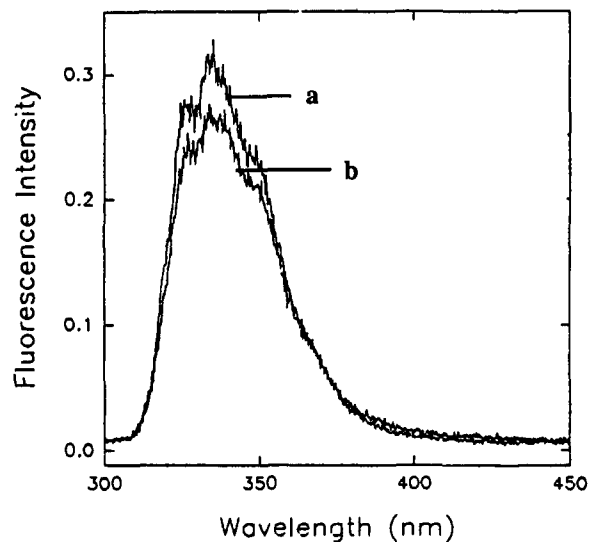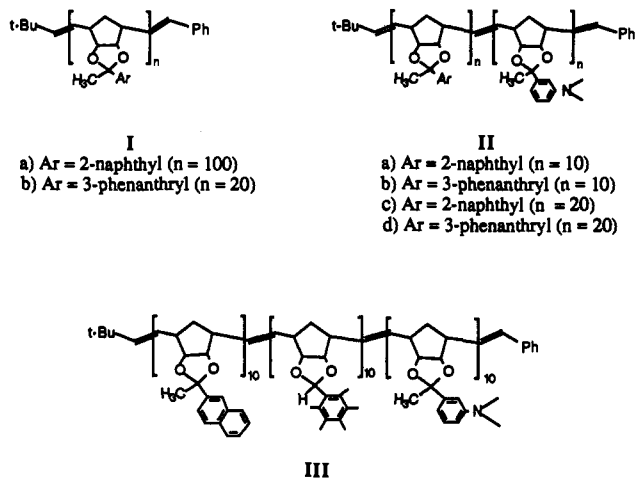

Figure 2. Steady-state fluorescence spectra in deaerated dichloromethane at ambient temperature: (a) Ia (10^{-5} M) and (b) naphthalene (10^{-4} M). Excitation wavelength = 284 nm.

neither interchain nor intrachain interactions form excimers between pendant naphthalene and dimethylamino units under the conditions of this experiment. This contrasts with the strong excimer (or exciplex) emissions resulting from intramolecular association along flexible polymer backbones that have been observed in all other chromophore-derivatized polymer systems reported to date.[1-3,5] Third, single photon counting measurements of homopolymer Ia show a single-exponential decay with an excited-state lifetime of 9.2 ns, which is indicative of only a single excited-state decay pathway.[9] A nonemissive exciplex resulting from polymer folding would instead lead to biexponential decay

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Communications to the Editor

I

a) Ar = 2-naphthyl (n = 100)
b) Ar = 3-phenanthryl (n = 20)

II

a) Ar = 2-naphthyl (n = 10)
b) Ar = 3-phenanthryl (n = 10)
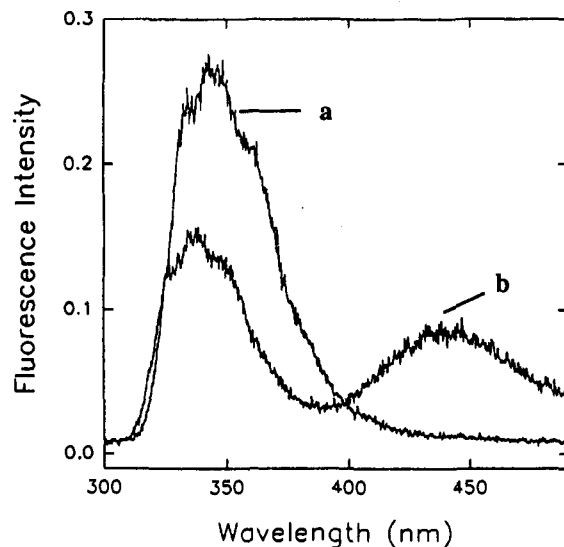c) Ar = 2-naphthyl (n = 20)
d) Ar = 3-phenanthryl (n = 20)

III

Figure 3. Steady-state fluorescence spectra in deaerated dichloromethane at ambient temperature: (a) **Ia** (10^{-5} M) and (b) **IIa** (10^{-5} M). Excitation wavelength = 284 nm.

kinetics. Thus, these polymers are rigid and uniform, at least on the time scale of the excited-state lifetime.

A photophysical analysis of diblock copolymer **IIa** in dichloromethane demonstrates vectorial energy migration preceding photoinduced electron transfer. Upon excitation at 284 nm, **IIa** shows a steady-state fluorescence spectrum indicative of two emissive species, naphthalene monomer and a naphthalene–dimethylaniline exciplex (440 nm) formed at the diblock interface, Figure 3. The emission from copolymer **IIa** from 330 to 360 nm (as naphthalene monomer) is virtually identical to that from homopolymer **Ia** in band shape and position. However, the fluorescence quantum yield for **IIa** is reduced by 35% (to 0.027 from 0.044 as measured for **Ia**, after correcting for trailing exciplex emission and overlapping absorption). The fractional fluorescence quenching of naphthalene monomer in a 10:10 copolymer would be less than or equal to 10% if no energy migration took place: that is, if quenching resulted only from random, but local, excitation of that chromophore at the diblock interface. The observed enhanced quenching requires efficient singlet energy migration to the naphthalene–dimethylaniline interface, where quenching occurs.

Intermolecular electron transfer and exciplex formation as a source of the observed fluorescence quenching have been eliminated by demonstrating the insensitivity of the intensity of exciplex formation on the concentration of **IIa** under the conditions of this measurement (concentrations between 10^{-6} and 10^{-5} M). The enhanced quenching in **IIa** must therefore derive solely from intramolecular energy or electron transfer.

Similar results were observed with diblock copolymer **IIb** containing phenanthrene and dimethylaniline pendant groups. As in **Ib**, discrete emissions could be observed for the phenanthrene monomer (345–395 nm) and the phenanthrene–dimethylaniline exciplex (450 nm). In **IIb**, the intensity of the phenanthrene monomer emission was reduced by 60% (compared with that in homopolymer **Ib**). The enhanced quenching in **IIb** over that observed in **IIa** can be explained by the difference in lifetimes of the two pendant arene absorbers. The fluorescence lifetimes of **Ia** and **Ib** are 9.2 and 16 ns, respectively. The ratio of the lifetimes of phenanthrene to naphthalene (1.74) correlates directly with the increased quenching by dimethylaniline observed in **IIb**.

Enhanced energy migration to the interface, rather than electron or hole migration, is likely to be responsible for the enhanced quenching.

The efficiency of excitation transport to the interface of the 10:10 diblock copolymers (**IIa** and **IIb**) can be statistically analyzed[10] by comparing the observed quenching to the average statistical number of chromophores through which energy must hop, assuming a Monte Carlo random walk, to reach the interface. For example, monomer quenching of 35% correlates with a random distribution of excitation energy among approximately three of the 10 chromophores (presumably, those closest to the interface) prior to quenching at the interface.

By the same analysis, a 20:20 diblock, with twice the number of excitable chromophores and twice the distance to the interface, should statistically show approximately half the quenching observed in a 10:10 diblock copolymer. The fluorescence spectra of diblock copolymers **IIc** and **IId** reveal monomer emission quenching of 15% in **IIc** (cf. **Ia**) and 27% in **IId** (cf. **Ib**). Thus, these polymers showed approximately half the fluorescence quenching of their 10:10 diblock copolymer analogs **IIa** and **IIb**, as predicted by a purely statistical analysis.

Supplementary Material Available: Synthetic procedures for the preparation of the monomers and polymers, together with spectral data for their characterization (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(9) The lifetime of the naphthyl-substituted monomer precursor of **1a** is also 9 ns. Substitution is known to shorten singlet lifetimes: e.g., τ_F of naphthalene is 100 ns, whereas that of methylnaphthalene is 59 ns.

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