Macromolecules **1993,** *26,* 1941–1946

Intramolecular Excimer Formation and Energy Transfer in Alternating Carbazole Copolymers

Yoshihiro Itoh,* Masakazu Nakada, Hideto Satoh, and Akira Hachimori

Institute of High Polymer Research, Faculty of Textile Science and Technology, Shinshu University, Ueda 386, Japan

Stephen E. Webber

Department of Chemistry and Biochemistry and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712

Received October 2, 1992; Revised Manuscript Received January 13, 1993

ABSTRACT: Alternating copolymers of *N*-vinylcarbazole (VCz) with diethyl fumarate (DEF), maleic anhydride (MAn), and citraconic anhydride (CAn) (a-CzEF, a-CzMAn, and a-CzCAn, respectively) were synthesized. The fluorescence spectra of a-CzEF and a-CzCAn changed as a function of the monomer feed ratios although all the copolymers had nearly 50 mol % of VCz content (f_{Cz}), indicating the presence of excimer-forming sites in the polymer chain. The copolymer obtained at $f_{\mathrm{Cz}} = 0.5$ in the monomer feed was found to be the most desirable "alternating" copolymer with the highest fluorescence quantum yield. Comparison of the spectral features for a-CzMAn and a-CzCAn showed that hindered groups on comonomers effectively restricted the excimeric interaction in copolymers. A small number of anthryl energy traps were covalently incorporated into a-CzEF and a random copolymer of VCz and methyl methacrylate with $f_{\mathrm{Cz}} = 0.5$ (r-CzMMA(50)) by terpolymerization with 9-anthrylmethyl methacrylate. Energy transfer to anthracene was more favorable in a-CzEF than in r-CzMMA(50). This result strongly suggests that longer-range energy transfer assisted by efficient energy migration is occurring in the alternating copolymer, which may be due in part to the large Förster radius for carbazole–carbazole for self-transfer (~2.1 nm).

Introduction

Singlet energy migration and excimer formation in aromatic polymers have been studied extensively.[1] Inhibition of excimer formation and other quenching processes is crucial not only for the design of "photon-harvesting" polymers but also for increasing our understanding of the complicated physical behavior of polymer systems. One can expect that in the former case energy transfer to traps would be facilitated[2] and that in the latter case the kinetic scheme in the excited states would be simplified.[3] In this context, a lot of effort has been directed to avoiding excimer formation in various types of polymers;[2] e.g., introduction of bulky groups on chromophores,[3,4] fixing of chromophores to the rigid polymer chain,[5] separation of chromophores from the main chain,[6,7] and alternation of chromophores.[8–10] Recently, Ito et al. demonstrated that poly[2-(9-carbazolyl)ethyl methacrylate] does not form an excimer even in a neat film, leading to efficient energy migration.[7] A successful alternative photon-harvesting polymer system was designed very recently by Morishima et al. in which hydrophobic association of naphthyl chromophores in aqueous solution, in spite of favorable excimer formation, enables the most rapid and efficient energy transfer in synthetic polymers reported so far.[11]

We have been investigating the photophysical properties of a series of amphiphilic alternating copolymers as promising candidates for photon-harvesting polymers.[2,9,10] In a previous paper, we reported that poly(9-vinylphenanthrene-*alt*-methacrylic acid) showed no self-quenching in organic solution, implying efficient energy migration.[10] Sensitization of the intramolecular energy traps (anthryl groups), however, was only slightly enhanced compared to the corresponding random copolymers. This may be due in part to the fact that phenanthrene (Phen) has a smaller Förster radius (R_0) for self-transfer (~0.9 nm).[12] This value is close to the average Phen–Phen separation in the alternating copolymer (0.6–0.8 nm)[10a] and is much smaller than that for transfer to anthracene (~2.2 nm),[12] which would lead to inefficient energy migration and exclusively to direct (single-step) transfer to traps. Thus a larger R_0 for self-transfer is desired for photon harvesting via singlet-state migration processes.[2]

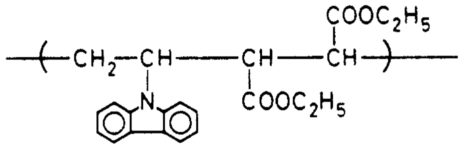
Our attention is now focused on alternating copolymers containing chromophores with larger R_0 values for self-transfer such as carbazole (~2.1 nm) and anthracene (~2.2 nm).[12] Shirota and co-workers have demonstrated that radical copolymerizations of *N*-vinylcarbazole (VCz) with electron-accepting monomers such as fumaronitrile, diethyl fumarate (DEF), and maleic anhydride (MAn) produce alternating copolymers.[13] They also reported that these polymers exhibit only monomer fluorescence.[14] However, energy migration and transfer processes in the above polymers have not been mentioned. In the present study, we compare the fluorescence properties of these types of alternating copolymers containing carbazolyl groups:[15] poly(VCz-*alt*-DEF) (a-CzEF),[14] poly(VCz-*alt*-MAn) (a-CzMAn),[16] and poly(VCz-*alt*-citraconic anhydride) (a-CzCAn). Intramolecular energy transfer to covalently bound anthryl traps is also examined.

Experimental Section

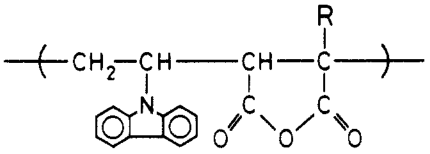
Materials. *N*-Vinylcarbazole (VCz; Nacalai Tesque) was recrystallized several times from *n*-hexane. Diethyl fumarate (DEF; Nacalai Tesque), citraconic anhydride (CAn; Wako Chemical), and methyl methacrylate (MMA; Wako Chemical) were distilled under reduced pressure. Maleic anhydride (MAn; Wako Chemical) was recrystallized twice from chloroform. 9-Anthrylmethyl methacrylate (AMMA) was prepared according to the literature.[17]

Benzene used for polymerization and tetrahydrofuran (THF) used for fluorescence measurements were both dried over sodium and distilled.

Copolymers and Terpolymers. Copolymers of VCz and DEF (a-CzEF) were prepared according to the method of Shirota et al.[14] with some modifications: A 20-mL benzene solution containing VCz and DEF in a known ratio (25 mmol in total) and 1 mol % (on the basis of total monomers) of 2,2′-azobis(isobutyronitrile) was evacuated by several freeze–pump–thaw



a-CzEF



R = -H a-CzMAn

-CH_3 a-CzCAn

cycles. Polymerizations were carried out at 60 °C for 1 h. The monomer conversion was kept under 10%. The polymerization solution was poured into a large excess of *n*-hexane followed by two more precipitations from THF into *n*-hexane.

The copolymers of VCz with MAn or CAn (a-CzMAn and a-CzCAn, respectively) were also prepared. In these cases, the copolymerization proceeded heterogeneously. The resulting polymers were collected by centrifugation and further purified by three precipitations from THF into *n*-hexane. Solubility behavior and GPC analysis for the alternating copolymers indicated no contamination of a detectable amount of the VCz homopolymer.[14,16]

Copolymerization of VCz and MMA (r-CzMMA(x): x denotes the VCz content in mol %) and terpolymerizations of VCz, DEF, or MMA, and AMMA (a-CzEF-A(y) and r-CzMMA-A(y): y denotes the AMMA content in mol %) were performed in a similar manner.

Characterization of Copolymers and Terpolymers. Composition of the copolymers and terpolymers was determined primarily by using absorption spectra.

Molecular weights of the polymers were estimated by using a Toyo Soda HLC-802A. Monodisperse polystyrene samples were used as standards.

Measurements. Steady-state fluorescence spectra were recorded at room temperature on a Hitachi 650-10S fluorescence spectrophotometer. Sample solutions were deaerated by bubbling with nitrogen for 15 min.

Fluorescence lifetime measurements were carried out either by using a Photochemical Research Associates single-photon-counting instrument or at the CFKR (Center for Fast Kinetics Research, The University of Texas at Austin) facilities. Details of instrumentation have been described elsewhere.[18]

Results and Discussion

Polymer Characterization. The results of the copolymerization of VCz and DEF are shown in Table I. The copolymer compositions for all a-CzEF samples are nearly equimolar over a wide range of the VCz mole fraction (f_{Cz}) in monomer feed, indicating that these polymers are alternating in nature. However, recent fluorescence studies have established that alternating radical copolymerizations result in the formation of a small fraction of consecutive diad sequences for one monomer depending on the monomer feed ratio.[18-20] The alternation tendency of copolymerization was checked conveniently by referring to the monomer reactivity ratios. The ratios determined from the Fineman–Ross plot for the VCz(M_1)–DEF(M_2) system were $r_1 = 0.013$ and $r_2 = 0.007$. The rather small values indicate a good tendency for alternation in a-CzEF; i.e., these polymers have few diad sequences for M_1M_1 and M_2M_2. In fact, the consecutive diad fractions for M_1M_1 (F_{11}) calculated from the reactivity ratios[19] were much smaller than those for poly(2-vinylnaphthalene-*alt*-MAn)[19] and poly(2-isopropenylnaphthalene-*alt*-MAn)[18] (Table I).

Table I
Preparation and Characterization of the Copolymers of VCz and DEF[a]

	f_{Cz}				
polymer	feed	polym[b]	yield, %	M_n[c]	F_{11}[d]
a-CzEF-1	0.10	0.49	1.0	1.8×10^4	0.0007
a-CzEF-2	0.17	0.49	1.9	2.0×10^4	0.001
a-CzEF-3	0.40	0.50	2.6	6.4×10^4	0.004
a-CzEF-4	0.50	0.52	3.0	1.0×10^5	0.007
a-CzEF-5	0.60	0.50	3.6	1.0×10^5	0.010
a-CzEF-6	0.90	0.53	6.3	1.2×10^5	0.056

[a] Polymerized in benzene at 60 °C: polymerization time, 1 h. [b] From absorption using PVCz as a standard. [c] Polystyrene equivalent number-average molecular weights determined by GPC. [d] Fraction of Cz–Cz diad (ref 19b).

Table II
Preparation and Characterization of the Copolymers of VCz with MAn and CAn[a]

	f_{Cz}		polym			
polymer	feed	polym	time, h	yield, %	M_n	I_{360}/I_{345}[b]
a-CzMAn-1	0.30	0.18	46	3.8	2.7×10^4	
a-CzMAn-2	0.39	0.36	43	6.6	4.4×10^4	
a-CzMAn-3	0.50	0.45	24	22	6.0×10^4	
a-CzMAn-4	0.60	0.47	22	20	6.4×10^4	
a-CzMAn-5	0.70	0.45	19	58	7.0×10^4	
a-CzCAn-1	0.40	0.46	28	9.6	3.0×10^4	1.09
a-CzCAn-2	0.50	0.51	24	28	4.2×10^4	1.00
a-CzCAn-3	0.64	0.51	5	15	5.8×10^4	1.01
a-CzCAn-4	0.80	0.51	5	21	5.2×10^4	1.10

[a] The conditions are the same as in Table I except the polymerization time. [b] Intensity ratio of the peak fluorescence at 360 nm to that at 345 nm.

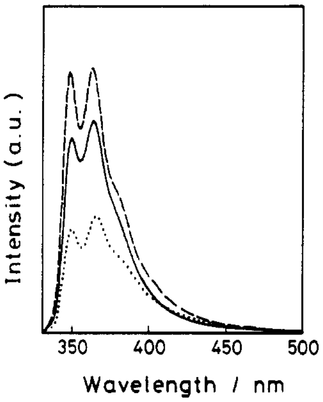


Figure 1. Steady-state fluorescence spectra of a-CzEF in THF at room temperature. f_{Cz} in the feed: (—) 0.10; (– –) 0.50; (- - -) 0.90. $[Cz]_{residue} = 6.1 \times 10^{-6}$ M. Excitation wavelength, 325 nm.

In Table II are summarized the results of the copolymerizations of VCz with MAn and CAn. In both systems, the polymerizations proceeded heterogeneously, while no precipitates were obtained when MAn and CAn were in a large excess in the feed.[21] The copolymers with $f_{Cz} \geq 0.5$ in the feed were likely highly alternating character. Although the reactivity ratios could not be determined for the present systems, the comparison of the copolymerizations for styrene–MAn and styrene–CAn systems implies that a-CzCAn has a somewhat lower tendency of alternation than a-CzMAn.[22]

Steady-State Fluorescence of a-CzEF. Figure 1 compares the fluorescence spectra of a-CzEF at various

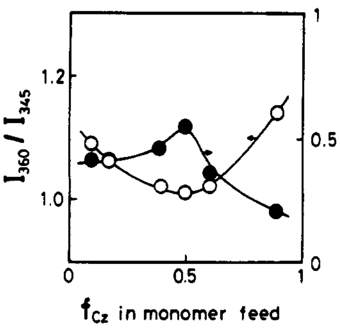


Figure 2. Dependences of the peak intensity ratio (I_{360}/I_{345}) (○) and the relative intensity at 345 nm (I_{rel}) (●) on f_{Cz} in the feed for a-CzEF. $[Cz]_{residue} = 6.1 \times 10^{-6}$ M. Excitation wavelength, 325 nm. I_{rel} is normalized to the intensity of r-CzMMA(1).

Table III
Fluorescence Decay Parameters for VCz Copolymers in THF[a]

polymer	λ_{em},[b] nm	τ_i/a_i, ns		
a-CzEF-4	350	0.9/0.26	8.7/0.39	20.4/0.35
a-CzEF-5	350	1.1/0.28	7.7/0.38	19.4/0.34
a-CzMAn-3	350	0.8/0.28	7.1/0.43	13.6/0.30
	370	1.2/0.39	9.2/0.57	26.2/0.04
a-CzCAn-2	350	1.2/0.46	6.5/0.42	12.1/0.13
	370	1.1/0.47	6.6/0.44	18.6/0.09
r-CzMMA(1)	350	10.5		
r-CzMMA(45)	350	0.9/0.20	10.3/0.61	18.7/0.20

[a] The decay curves are analyzed by using the equation; $I(t) = \sum a_i \exp(-t/\tau_i)$: excitation wavelength, 293 nm. [b] Wavelength at which fluorescence decays were monitored.

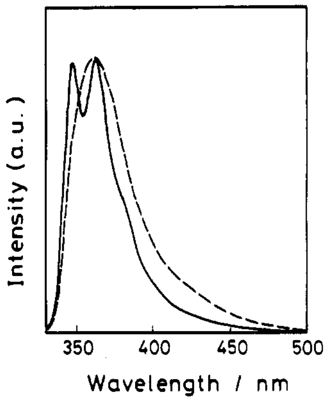


Figure 3. Steady-state fluorescence spectra of a-CzCAn-2 (—) and a-CzMAn-3 (- -) (f_{Cz} = 0.5 in the feed) in THF at room temperature. $[Cz]_{residue} = 6.1 \times 10^{-6}$ M. Excitation wavelength, 328 nm.

monomer feed ratios in THF. All the copolymers showed a structured emission similar to that of *N*-ethylcarbazole, while the spectra were slightly broadened and blue-shifted by ca. 5 nm compared with that for the latter. These are consistent with the results reported by Shirota et al.[14] They have concluded that a-CzEF exhibits only monomer fluorescence. In the present study, however, the spectra apparently depended on f_{Cz} in the feed; i.e., in the spectrum of a-CzEF obtained at either a higher or lower f_{Cz} in the feed, a slightly broad emission appeared in the longer wavelength region (>360 nm) along with a decrease in the intensity at the emission maximum. These facts strongly suggest the presence of excimer-forming sites in a-CzEF.

In Figure 2, the ratios of the peak intensity at 360 nm to that at 345 nm (I_{360}/I_{345}) were plotted as a function of f_{Cz} in the feed. The former peak includes the contribution of second excimer emission,[23] if any. The relative fluorescence intensities at 345 nm (I_{rel}), normalized to that of r-CzMMA(1), are also plotted. The opposite tendency of I_{360}/I_{345} and I_{rel} supports the idea that the quenching may be due to excimer formation. The copolymer obtained at f_{Cz} = 0.5 in the feed (a-CzEF-4) had the maximum fluorescence intensity and the minimum I_{360}/I_{345} ratio, indicating that this polymer is the most desirable one. However, there still remained some quenching sites in the above polymer because the fluorescence intensity was lower than that of the model polymer (r-CzMMA(1); Figure 2) and the fluorescence decay curve for the monomer emission had a shorter decay time (Table III). Unfortunately this would lower the efficiency of photon harvesting in the copolymer to some extent. A similar tendency was observed for a-CzCAn (see below).

It is interesting to note that the concave-shaped dependence of the peak intensity ratio on the monomer feed for a-CzEF contrasts the tendency for the same type of alternating copolymers containing styryl and naphthyl chromophores. For this polymer system the intensity ratio of excimer to monomer fluorescence (I_E/I_M) increases with the chromophore monomer feed.[19,20] It seems reasonable to assume that intramolecular excimer formation in a flexible polymer chain in a dilute solution occurs predominantly by the nearest-neighbor interaction.[24] In such a case, excimer-forming sites should be located in the diad sequence of chromophore monomers, the fraction of which (F_{11}) is obtained as a function of the monomer feed ratio as described above, and thus the I_E/I_M ratio should increase monotonously with the monomer feed ratio. This is ordinarily the case for many aromatic polymers. Thus the peculiar dependence observed in Figure 2 would lead to the following possibilities: (1) Excimer formation occurs by non-nearest-neighbor interaction in the alternating sequences of a-CzEF. (2) Excimer-forming sites are located in the VCz–VCz diad sequences, but the number of these sites are not directly related to the diad fraction. It should be noted here that the intensity of excimer emission increased with the VCz monomer feed, i.e., the VCz–VCz diad fraction, in the VCz random copolymer, r-CzMMA(x), and the alternating copolymers of VCz and fumarate derivatives, in which alternation was quite low.[25] This means that the VCz moieities form an excimer preferentially by nearest-neighbor interactions in the copolymers. Therefore, although it is difficult to rule out the former possibility, we believe that efficient energy migration occurs to very few excimer-forming sites formed in the VCz–VCz diad sequences of a-CzEF. However, we still have no concrete interpretation for the minimum intensity ratio of a-CzEF-4 (f_{Cz} = 0.5 in the feed). This might be related to the tacticity of polymers, which significantly affects excimer formation for carbazole chromophores.[1,3] Our lack of information on the microstructure of the alternating copolymers does not permit further discussion.

Steady-State Fluorescence of a-CzMAn and a-CzCAn. Figure 3 shows the fluorescence spectra of a-CzMAn-3 and a-CzCAn-2 (f_{Cz} = 0.5 in the feed) in THF. The spectral features of a-CzCAn were almost the same as those of a-CzEF, and the intensity ratio of the two peaks (I_{360}/I_{345}) also showed a similar dependence on the monomer feed (Table II). These results indicate that there are a very few excimer-forming sites in a-CzCAn as well as in a-CzEF.

On the other hand, any a-CzMAn produced by different monomer feed ratios exhibited only a broad excimeric emission at ca. 360 nm. This emission is similar to an unstable second excimer observed in a sterically hindered poly(VCz), poly(3,6-di-*tert*-butyl-9-vinylcarbazole), reported by Ito et al.[3] They attributed this to formation of a slightly overlapping excimer site in syndiotactic diads

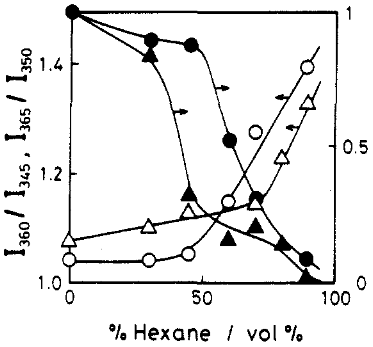


Figure 4. Peak intensity ratios (I_{360}/I_{345} or I_{365}/I_{350}) (○,△) and relative intensities (I_{rel}) (●,▲) of a-CzEF-4 and r-CzMMA(55) in the THF–*n*-hexane mixtures: (○,●) a-CzEF-4; (△,▲) r-CzMMA-(55). $[Cz]_{residue} = 1.9 \times 10^{-6}$ M. The abscissa indicates the volume fraction of *n*-hexane in percent. I_{rel} is normalized to the intensity of that in THF.

in the polymer chain and to efficient energy migration to this site. The former emission, however, was somewhat broader with a slight tailing probably because of some contribution of sandwich excimer emission. It should be noted that in rigid solution at 77 K excimeric emission for a-CzMAn was still observed. This is indicative of the presence of preformed second excimer sites in a-CzMAn.

The marked difference in the spectral features between a-CzCAn and a-CzMAn is obviously due to the steric hindrance of the methyl group on CAn. Inspection of the molecular model reveals that there is some overlapping of the neighboring carbazole chromophores in the alternating sequences of a-CzMAn[26] and that the methyl group on CAn blocks this overlapping. Thus excimer formation would occur in both the VCz–VCz diad and VCz–MAn alternating sequences in a-CzMAn and would do primarily in the diad sequences in a-CzCAn. Furthermore, the methyl substituents would restrict the conformational change required to form the excimer. Similar situations were encountered for the VCz random copolymers; i.e., excimer emission for poly(VCz-*co*-methyl methacrylate) (r-CzMMA(*x*)) was rather smaller than that for poly(VCz-*co*-methyl acrylate) (data not shown). It may thus be said that hindered groups on comonomers play an important role to disfavor excimeric interactions in copolymers.

Fluorescence Lifetimes. The decay curves of fluorescence for all the copolymers showed a deviation from simple exponential behavior except for r-CzMMA(1). The lifetimes obtained from a three-exponential fit are listed in Table III. There was a longer-lifetime component (τ > 12 ns) whose lifetime became longer when emission was monitored at longer wavelength. This is additional evidence that excimer formation is occurring in all the alternating copolymers used here.

Solvent Effect on Excimer Formation. It has been established that in solution excimer formation in polymers depends strongly on the solvent power, which modifies the polymer coil dimensions.[27] In the present case, different solvent effects on the fluorescence spectra of the alternating and random copolymers were observed. The effect of adding *n*-hexane, a nonsolvent, to the THF solutions of a-CzEF-4 and r-CzMMA(55) is shown in Figure 4.[28] As expected, the I_{rel} values decreased and the peak intensity ratios (I_{360}/I_{345} and I_{365}/I_{350} for a-CzEF-4 and r-CzMMA(55), respectively) increased with the hexane content in the mixtures because contraction of the dimensions of the polymer coil enhanced excimer formation and thus self-quenching. These values for r-CzMMA-(55) were affected at a lower hexane content than those for a-CzEF-4 because of the lower solubility of the former polymer in the mixtures.[29] It is interesting to note here that for r-CzMMA(55) the change in the I_{rel} value shifted to a lower hexane content than that in the I_{365}/I_{350} ratio. This clearly indicates that the coil collapse of r-CzMMA-(55) induces some quenching processes other than excimer formation. Both quenching and excimer formation are due to the VCz–VCz interaction, leading to a larger decrease of the fluorescence quantum yield in a lower hexane content. Such discrepancy was also observed for the dependences of the I_{rel} and I_{365}/I_{350} on the copolymer composition of r-CzMMA(*x*) (data not shown). The I_{rel} value for a-CzEF, on the other hand, decreased simultaneously with the increase of I_{360}/I_{345}, and the excimer emission in the hexane-rich mixture was enhanced. These findings imply that there are few quenching sites other than excimer-forming sites in a-CzEF and that more efficient energy migration, which is facilitated by contracting the dimensions of the polymer coil, occurs solely to these excimer sites, even though they are present in very low concentrations.

Table IV
Preparation and Characterization of Anthracene-Loaded Alternating and Random Copolymers[a]

	in feed, mol %		in polym, mol %		
polymer	f_{Cz}	f_{AMMA}	f_{Cz}	f_{AMMA}	M_n
a-CzEF	50.0		52.4		1.0×10^5
a-CzEF-A(0.3)	49.8	0.4	50.5	0.26	2.0×10^4
a-CzEF-A(0.7)	49.4	1.2	50.9	0.75	3.2×10^4
a-CzEF-A(1.3)	49.0	2.0	51.3	1.28	1.0×10^4
r-CzMMA(45)	69.8		44.7		3.3×10^5
r-CzMMA-A(0.3)	74.9	0.2	50.6	0.27	6.4×10^4
r-CzMMA-A(0.7)	74.7	0.4	50.9	0.74	2.5×10^4
r-CzMMA-A(1.4)	74.6	0.6	50.6	1.35	1.7×10^4

[a] The polymerization conditions are the same as in Table I except the polymerization time (3–6 h).

Intramolecular Singlet Energy Transfer in Anthracene-Loaded Polymers. Alternating and random copolymers with $f_{Cz} = 0.5$ were loaded with small amounts of anthryl traps (<1.5 mol %) by terpolymerization with 9-anthrylmethyl methacrylate (AMMA). The resulting terpolymers were abbreviated as a-CzEF-A(*y*) and r-CzMMA-A(*y*), respectively, where *y* denoted the AMMA content in the terpolymer in mol %. Typical results of the terpolymerizations are shown in Table IV. Introduction of AMMA only slightly affected the VCz content in the terpolymers and their spectral shape. The molecular weight was decreased, presumably because of the lower polymerizability of AMMA. Therefore, it seems likely that the anthryl groups are randomly distributed in the terpolymers and that the coexistence of AMMA scarcely disturbs the alternation in a-CzEF.

The efficiency of energy transfer (χ) can be determined by using the equation[2]

$$\chi = [(I_A(\lambda)/I_A(\lambda_A))f_A(\lambda_A) - f_A(\lambda)]/f_D(\lambda) \qquad (1)$$

where $I_A(\lambda)$ and $I_A(\lambda_A)$ are the fluorescence intensities of the acceptor excited at the wavelength (λ) where the donor absorbs light and at the wavelength (λ_A) where only the acceptor does, respectively, and f_D and f_A are the fractions of incident light absorbed by the donor and acceptor, respectively.

In Figure 5, the χ values for a-CzEF-A(*y*) and r-CzMMA-A(*y*) are plotted against the mole fraction of AMMA in the terpolymer (f_{AMMA}). A linear relationship was obtained between χ and f_{AMMA} for r-CzMMA-A(*y*) at up to ca. 1.5 mol % of f_{AMMA}. On the other hand, energy transfer in a-CzEF-A(*y*) was more effective than that in r-CzMMA-A(*y*), and the plot showed an asymptotic curvature. These

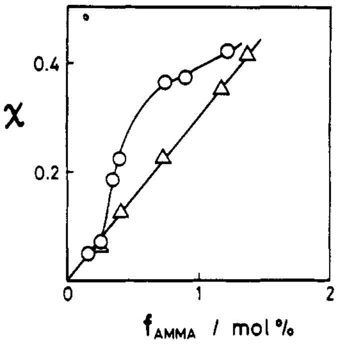


Figure 5. Energy transfer efficiency (χ) of the copolymers with different AMMA contents (f_{AMMA}) in THF. (○) a-CzEF-A(y); (△) r-CzMMA-A(y). $[Cz]_{residue} = 9.4 \times 10^{-6}$ M.

Table V
Förster Radii for Phenanthrene and Carbazole Chromophores (nm)[a]

donor	R_0^{DA}	R_0^{DD}	R_{DA}^0
phenanthrene	2.2	0.88	~1.8
carbazole	2.8	2.1	~0.9

[a] See text; acceptor, anthracene; from ref 12.

results imply that a longer range of energy transfer can occur in a-CzEF-A(y) and that the reactive spheres contributed to transfer overlap at higher f_{AMMA}. Here we must consider the fact that the average number of AMMA per polymer chain was estimated to be less than 1 for a-CzEF-A(y) (ca. 0.2–0.5) except for a-CzEF-A(0.7) (ca. 1.3) and to be larger than 1 for r-CzMMA-A(y) (ca. 1.2–1.5). The calculated χ values would then underestimate the efficiencies of intramolecular transfer for the former polymers. Therefore, it can be safely concluded that energy transfer efficiency in the alternating copolymers is higher than that in the random copolymers. In contrast, no enhanced transfer efficiency was observed for the alternating phenanthrene copolymers.[10a] Such a drastic difference can be ascribed in part to a larger R_0 value of carbazole for self-transfer.

If energy hopping, or migration, between the same chromophores occurs by the Förster mechanism, the ratio of the rate constants of energy hopping (k_{mig}) to energy transfer (k_{ET}) is given by[30]

$$k_{mig}/k_{ET} = (R_0^{DD}/R_{DD})^6/(R_0^{DA}/R_{DA})^6 \tag{2}$$

where R_0^{DD} and R_0^{DA} are the Förster radii for self-transfer and for transfer to the acceptor, respectively, and R_{DD} and R_{DA} are the distance between the donor chromophores and that between the donor and acceptor chromophores, respectively. We may use the Förster radii reported by Berlman (Table V).[12] If the average chromophore-chromophore distance in the alternating copolymers (R_{DD}) is 0.7 nm,[10a] then the critical R_{DA} values (R_{DA}^0), defined as quenching radii within which only a single-step Förster transfer occurs to the trap, can be calculated to be ca. 1.8 nm for the alternating phenanthrene polymer and ca. 0.9 nm for the carbazole polymer, respectively. Although these values are very approximate, it is clear that in the latter polymer energy transfer from the chromophores close to the anthryl traps can still be facilitated by energy hopping or migration. In other words, a lot of chromophores around the traps in a-CzEF-A contribute to energy transfer via energy migration.

We previously supposed that excited energy can migrate over a large fraction of the polymer chain in alternating copolymers because of the absence of traps and that random copolymers have excimer-like traps and isolated chromophore sequences with limited lengths, which would allow only a short-range of energy migration.[10a] The former situation would result in the increase of the energy transfer distance; i.e., the reactive spheres are extended, while in the latter case the distance would be limited. In addition, it is reasonable to consider that such enlargement is more enhanced for chromophores with a larger R_0^{DD} value. This may be the case for the alternating carbazole copolymers.

Table VI
Fluorescence Decay Parameters for Anthracene-Loaded VCz Copolymers in THF[a]

polymer	λ_{em},[b] nm	τ_i/a_i, ns			
a-CzEF-A(0.7)	350	0.8/0.41	5.9/0.36	16.8/0.23	
	460	0.3/−1.24	2.0/−1.85	7.7/3.84	23.2/0.25
r-CzMMA-A(0.7)	350	0.1/0.34	1.3/0.27	7.2/0.29	16.1/0.10
	460	0.3/−0.76	2.1/−0.73	7.6/2.34	30.0/0.15

[a] The decay curves are analyzed by using the equation $I(t) = \sum a_i \exp(-t/\tau_i)$; excitation wavelength, 293 nm. [b] Wavelengths at which fluorescence decays were monitored.

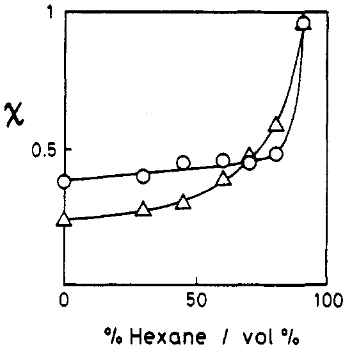


Figure 6. Energy transfer efficiency (χ) for a-CzEF-A(0.7) (○) and r-CzMMA-A(0.7) (△) in the THF–n-hexane mixtures. $[Cz]_{residue} = 9.4 \times 10^{-6}$ M. The abscissa indicates the volume fraction of n-hexane in percent.

Intramolecular energy transfer to the anthryl traps was confirmed by the time-dependent fluorescence. Table VI gives the multiexponential fitting parameters. The decay curves for the sensitized Anth fluorescence monitored at 460 nm had both rising components ($\tau \leq 2$ ns) and slowly-decaying components ($\tau > 20$ ns) along with the decrease of the carbazole fluorescence lifetimes monitored at 350 nm. These clearly indicate that energy transfer occurring in the nanosecond time region. Interestingly, the longest-lifetime component for the sensitized Anth fluorescence decayed faster in a-CzEF-A(0.7) ($\tau \sim 23$ ns) than in r-CzMMA-A(0.7) ($\tau \sim 30$ ns). This might be the result of a slightly faster transfer in the former polymer.

The effect of polymer coil shrinkage on the energy transfer efficiency was also investigated (Figure 6). The χ value for a-CzEF-A(0.7) changed very slightly with the hexane content up to 80 vol %, and above this content is increased steeply. This is unexpected because the addition of 50 vol % of hexane already begins to collapse the polymer coil, leading to enhanced excimer formation and self-quenching (Figure 4). As we speculated above, however, if the reactive spheres for energy transfer in a-CzEF-A(0.7) overlap each other to some extent, i.e., there exist a lot of carbazole chromophores within these spheres, then some contraction of coil dimensions would not appreciably affect a long range of the energy transfer process in spite of facilitation of excimer formation, which is a short range of the photophysical process. Addition of more than 80 vol % of hexane may bring all the chromophores within a distance comparable to the Förster radius, which enables almost perfect transfer to the anthryl traps. In the case of r-CzMMA-A(0.7), on the other hand, the χ value gradually increased with the hexane content probably because collapsing the polymer coil brought the chromophores in limited amounts into the smaller reactive spheres.

Conclusion

The fluorescence spectra of all the alternating copolymers of *N*-vinylcarbazole and the three acceptor monomers prepared in the present study showed an excimeric emission, which depended on the monomer feed ratios and on the steric hindrance of comonomers. The solvent effect on the fluorescence spectra implied that the alternating copolymers have few quenching sites other than excimer-forming sites and that efficient energy migration to these small numbers of sites is occurring. These advantages also enabled intramolecular energy transfer to the anthryl traps to be more favorable than the corresponding random copolymers. The contribution of energy migration to the anthryl sensitization may be due in part to a larger Förster radius for self-transfer for carbazole chromophores. Therefore, it can be concluded that the chromophores having the largest R_0 value and showing no self-quenching are desired for the singlet-state photon harvesting in synthetic polymer systems.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research (No. 02750630) from the Ministry of Education, Science and Culture, Japan. S.E.W. acknowledges the donors of the National Science Foundation Polymers Program (Grant DMR-9000562) and the Robert A. Welch Foundation (Grant F-356). We thank Drs. K. Kamioka and D. J. Kiserow of The University of Texas at Austin for the lifetime measurements.

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