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Chemistry of Excited Complexes in Copolymers Containing Phenanthrene and *N,N*-Dimethylaniline Moieties. Effects of Chemical Structure on the Intramolecular Exciplex Formation, Its Emission Properties, and Electron Transfer to Dicyanobenzene

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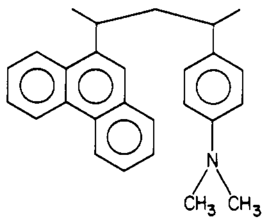
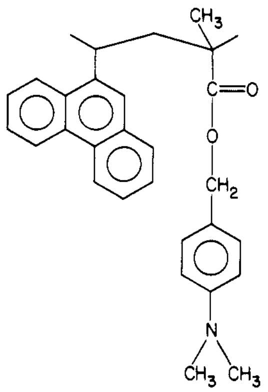
ABSTRACT: The formation and emission properties of intramolecular exciplexes in some vinyl copolymers containing phenanthrene and *N,N*-dimethylaniline moieties were studied. The monomers used were $CH_2{=}CH$-phenanthryl (VPh), $CH_2{=}C(CH_3)COOCH_2$-phenanthryl (PhMMA), $CH_2{=}CH$-DMA (DMAS), and $CH_2{=}C(CH_3)COOCH_2$-DMA (DMAMMA), where Ph and DMA are 9-phenanthryl and 4-(dimethylamino)phenyl groups, respectively. Poly(VPh-*co*-DMAS) was found to exhibit an intense intramolecular exciplex fluorescence, whereas poly(VPh-*co*-DMAMMA), poly(PhMMA-*co*-DMAS), and poly(PhMMA-*co*-DMAMMA) showed only a weak exciplex fluorescence. In poly(VPh-*co*-DMAMMA) the exciplex formation was poor, and in the PhMMA-containing copolymers, the phenanthrene monomer fluorescence was quenched effectively by the DMA chromophores, but the exciplex formed had low fluorescence quantum yields and short fluorescence lifetimes. The electron-transfer reactions in these copolymers + *p*-dicyanobenzene systems were also studied by flash photolysis. The amounts of *p*-dicyanobenzene anion radical detected in these systems decreased in the order poly(VPh-*co*-DMAS) > poly(VPh-*co*-DMAMMA) > poly(PhMMA-*co*-DMAS) ≅ poly(PhMMA-*co*-DMAMMA).

Introduction

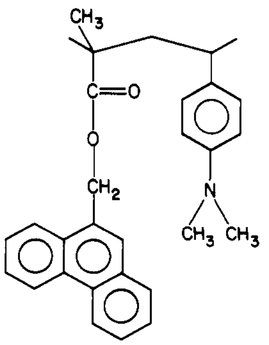
Many investigations on electronic energy migration, electronic energy transfer, and intramolecular excited-complexation form in synthetic polymers have been reported especially over the past decade. Polymers capable of energy migration and exciplex formation would be promising as photosensitizers in the electron-transfer reaction for the storage of light energy. We have studied the formation of intramolecular exciplex and electron transfer from exciplex to electron acceptors in aromatic vinyl copolymer systems.[1-4] Studies on photophysical processes in some phenanthrene-containing vinyl polymers have been reported.[5-7] These polymers showed no distinct low-energy broad-band intramolecular excimer emission but showed electronic energy migration. In a previous paper,[2] the formation of an intramolecular exciplex in 9-vinylphenanthrene-*p*-(dimethylamino)styrene copolymer and the photoinduced electron transfer from the copolymer to *p*-dicyanobenzene were studied. The emission properties and the oxidation potential of the exciplex were studied in comparison with those of a biochromophoric model compound, 1-[4-(dimethylamino)phenyl]-3-(9-phenanthryl)propane.[3,4] In the present paper, we report on the emission properties of vinyl copolymers in which phenanthrene and/or *N,N*-dimethylaniline chromophores were separated from the main chains by an intervening carboxymethylene group ($COOCH_2$). The results are discussed in relation to the relative geometry of the chromophores. The electron-transfer reactions in copolymer + *p*-dicyanobenzene systems were also studied by flash photolysis. The copolymers used in this study are as follows:



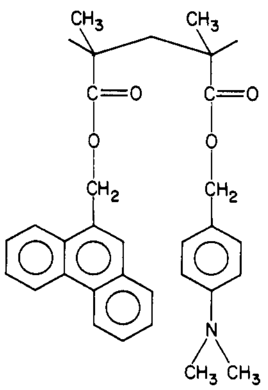
poly(VPh-*co*-DMAS)



poly(VPh-*co*-DMAMMA)



poly(PhMMA-*co*-DMAS)



poly(PhMMA-*co*-DMAMMA)

where DCB = *p*-dicyanobenzene, DMA = *N,N*-di-

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Table I
Radical Copolymerization[a] of Phenanthrene-Containing Monomer (M_1) with *N*,*N*-Dimethylaniline-Containing Monomer (M_2)

polymer	$[M_1]/([M_1] + [M_2])$	polymn time, h	conv, %	$d[M_1]/(d[M_1] + d[M_2])$	mol wt
poly(VPh)[b]	1.00	17	35.2	1.00	
poly(VPh-*co*-DMAS)(59)[b]	0.40	17	26.5	0.59	15500
poly(VPh-*co*-DMAMMA)(25)	0.10	16	20.1	0.25	24500
poly(VPh-*co*-DMAMMA)(50)	0.30	16	13.6	0.50	15000
poly(VPh-*co*-DMAMMA)(67)	0.50	16	15.0	0.67	13600
poly(VPh-*co*-DMAMMA)(80)	0.70	16	18.0	0.80	13600
poly(PhMMA)	1.00	2	43.6	1.00	128000
poly(PhMMA-*co*-DMAS)(25)	0.10	16	24.7	0.25	22000
poly(PhMMA-*co*-DMAS)(50)	0.50	3	8.7	0.50	51000
poly(PhMMA-*co*-DMAMMA)(48)	0.35	2	21.2	0.48	80000
poly(PhMMA-*co*-DMAMMA)(60)	0.50	2	28.9	0.60	90000
poly(PhEMA)	1.00	3.17	67.8	1.00	62000
poly(PhEMA-*co*-DMAS)(43)	0.50	3.25	17.7	0.43	42000
poly(PhEMA-*co*-DMAMMA)(52)[c]	0.50	6.83	78.5	0.52	96000

[a] [AIBN] = 5×10^{-3} M, $[M_1] + [M_2] = 0.5$ M. [b] $[M_1] + [M_2] = 0.8$ M. [c] $[M_1] + [M_2] = 0.3$ M.

methylaniline, DMAMMA = [4-(dimethylamino)phenyl]methyl methacrylate, DMAMP = [4-(dimethylamino)phenyl]methyl pivalate, DMAS = *p*-(dimethylamino)styrene, EtPh = 9-ethylphenanthrene, Ph = phenanthrene, PhEMA = 2-(9-phenanthryl)ethyl methacrylate, PhEP = 2-(9-phenanthryl)ethyl pivalate, PhMMA = 9-phenanthrylmethyl methacrylate, PhMP = 9-phenanthrylmethyl pivalate, and VPh = 9-vinylphenanthrene.

Experimental Section

Monomers. 9-Vinylphenanthrene (VPh) was prepared as described in the preceding paper.[2]

9-Phenanthrylmethyl Methacrylate (PhMMA). 9-Phenanthrylmethanol was prepared according to the method of Lambert.[8] The methacrylate was prepared by the method of Guillet[6] except that K_2CO_3 was used instead of triethylamine: yield 23.5%; mp 70.6–73.8 °C (lit.[9] mp 74–76 °C).

2-(9-Phenanthryl)ethyl Methacrylate (PhEMA). 2-(9-Phenanthryl)ethanol was prepared according to the method of Bergman.[10] The methacrylate was prepared by dropwise addition of 1.9 g (0.018 mol) of methacryloyl chloride in 10 mL of dry THF to a solution of 2.5 g (0.011 mol) of 2-(9-phenanthryl)ethanol, 1.5 g of triethylamine, and 10 mL of dry THF at 0 °C. The reaction mixture was stirred for 1 h at room temperature, and the amine salt was filtered off. After evaporation of volatile materials the residue was chromatographed on silica gel with hexane as eluent and recrystallized from hexane to yield 1.2 g (36.7%) of white needles: mp 55.2–55.9 °C. Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.76; H, 6.21. Found: C, 82.76; H, 6.24. ^{1}H NMR ($CDCl_3$) δ 1.92 (s, 3 H, CH_3), 3.47 (t, 2 H, CH_2), 4.55 (t, 2 H, OCH_2), 5.52 (s, 1 H, —CH=), 6.08 (s, 1 H, —CH=), 7.4–9.0 (m, 9 H, aromatic H); EIMS (70 eV), *m*/*e* (relative intensity) 290 (8), 205 (20), 204 (100), 203 (24), 191 (23), and 189 (11).

[4-(Dimethylamino)phenyl]methyl methacrylate (DMAMMA) was prepared according to the method of Hrabak[11] in 48% yield: mp 39.6–40.9 °C (lit.[11] mp 39 °C).

p-(Dimethylamino)styrene (DMAS) was prepared as described in the preceding paper.[1]

Polymers. The polymerization of VPh- and DMA-containing monomers was carried out in benzene and that of other phenanthrene-containing monomers and DMA-containing monomers in dioxane. These polymerizations were initiated by AIBN at 60 °C after degassing by four freeze–pump–thaw cycles on a vacuum line. The polymers were isolated by precipitation with methanol or hexane and purified by reprecipitation from benzene solution with methanol (VPh-containing polymers) or from dioxane solution with hexane (PhMMA- or PhEMA-containing polymers) and dried under reduced pressure. Results are listed in Table I, where the copolymer compositions are determined by elemental analysis, and the molecular weights are evaluated by the peak top positions of GPC diagrams in THF and calibrated by polystyrene standards.

Other Materials. 9-Phenanthrylmethyl pivalate (PhMP)[6] was prepared from 9-phenanthrylmethanol by employing the procedure of PhEMA synthesis: mp 53.5–54.8 °C.

2-(9-Phenanthryl)ethyl pivalate (PhEP) was synthesized similarly from 2-(9-phenanthryl)ethanol and pivaloyl chloride: yield 47%; mp 86.2–87.5 °C. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.14; H, 7.26. ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9 H, CH_3), 3.42 (t, 2 H, CH_2), 4.46 (t, 2 H, OCH_2), 7.4–8.9 (m, 9 H, aromatic ring H); EIMS (70 eV), *m*/*e* (relative intensity) 306 (7), 205 (26), 204 (100), 203 (20), and 191 (12).

9-Ethylphenanthrene (EtPh) was the same as used in a previous work.[4]

[4-(Dimethylamino)phenyl]methyl pivalate (DMAMP) was synthesized by the method used for DMAMMA. The crude product was purified by column chromatography followed by recrystallization from petroleum ether: yield 24.2%; mp 25.1–25.8 °C. Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.45; H, 9.00; N, 5.95. Found: C, 71.24; H, 9.05; N, 5.91. ^{1}H NMR ($CDCl_3$) δ 1.19 (s, 9 H, CH_3), 2.94 (s, 6 H, $N(CH_3)_2$), 5.01 (s, 2 H, CH_2), 6.5–7.4 (m, 4 H, aromatic ring H); EIMS (70 eV), *m*/*e* (relative intensity) 235 (31), 134 (100), and 119 (11).

Phenanthrene was a zone-refined reagent (Tokyo Chemical Ind. Co.). DMA was purified from a commercial product by fractional distillation. *p*-Dioxane was refluxed over sodium and then distilled through a Widmer column. DMF was purified by removing water as a benzene azeotrope and by distillation through a Widmer column. DCB was recrystallized from acetone.

Measurement. Fluorescence spectra were recorded on a Shimadzu RF-502A spectrofluorimeter and a Union FS-401 spectrofluorimeter at 25 °C or at room temperature. Solution samples, whose absorbance at excitation wavelength was ca. 0.1, were made oxygen free by purging with N_2 gas or by freeze–pump–thaw cycles on a vacuum line. For fluorescence quantum yield (Φ) measurements, a solution of quinine sulfate ($\Phi = 0.55$) in 1 N H_2SO_4 optically matched with the sample solutions at excitation wavelengths was used as the reference sample. Φ was measured by comparing the area under the emission peak (vs. cm^{-1}) to the area under that of the reference sample according to the equation

$$\Phi = \Phi_r \frac{\text{area}}{\text{area}_r} \frac{A_r}{A} \frac{n^2}{n_r^2}$$

where A is the absorbance at excitation wavelength, n is the refractive index of the pure solvent, and subscript r denotes the reference sample.

Lifetime was measured by the pulse method with a small Blumlein-type nitrogen gas laser as described previously.[2,3] A sample dioxane solution was sealed in a 3-mm Pyrex glass capillary tube after degassing by four freeze–pump–thaw cycles on a vacuum line. The fluorescence decay curve was determined with a monochrometer (Union FS401), using a photomultiplier (Hamamatsu TV 1P28) and an oscilloscope (Tektronix 485). The exciplex and phenanthrene fluorescences were monitored at 440 and 370 nm, respectively. About 100 traces of fluorescence decay curve were taken photographically and analyzed by single-exponential kinetics.[3]

The flash photolysis apparatus was the same as used in previous work.[2] The cylindrical quartz cell was about 1 cm in diameter

Table II
Fluorescence Quantum Yield[a] and Lifetime of Phenanthrene and DMA Copolymers in Dioxane

copolymer	Φ_M	Φ_E	τ_E, ns
poly(VPh-*co*-DMAS)(59)	0.00_7	0.12_0	52
poly(VPh-*co*-DMAMMA)(50)	0.05_7	0.01_9	42
poly(PhMMA-*co*-DMAS)(50)	0.00_3	0.00_7	8.4
poly(PhMMA-*co*-DMAMMA)(60)	0.00_3	0.00_3	7.0
poly(PhEMA-*co*-DMAS)(43)	0.01_8	0.06_2	50
poly(PhEMA-*co*-DMAMMA)(52)	0.00_6	0.11_3	51
poly(PhMMA)	0.08_6		43 (τ_M)
PhMP	0.09_5		46 (τ_M)

[a] Quinine sulfate in 1 N H_2SO_4 was used as a reference sample.

and 10 cm in length, and a glass plate with 50% transmittance at 325 nm was used as a cutoff filter.

Results and Discussion

Emission Properties of Copolymers. In Figure 1 are shown the fluorescence spectra of copolymers poly(VPh-*co*-DMAS) and poly(VPh-*co*-DMAMMA) obtained by the selective excitation of the VPh portion at 352 nm (λ_{max}). Poly(VPh-*co*-DMAS) was found to exhibit an intense and broad intramolecular exciplex fluorescence at ca. 440 nm together with a weak phenanthrene monomer fluorescence,[2] whereas poly(VPh-*co*-DMAMMA) showed only a weak exciplex fluorescence, which is shown in curve d, obtained by subtracting the poly(VPh) fluorescence spectrum (curve c) from the spectrum of poly(VPh-*co*-DMAMMA) (curve b) normalized at the phenanthrene monomer fluorescence.

The fluorescence spectra of copolymers poly(PhMMA-*co*-DMAS) and poly(PhMMA-*co*-DMAMMA) obtained by the selective excitation of the PhMMA portion at 348 nm (λ_{max}) showed an exciplex fluorescence at ca. 440 nm (Figure 2).

Since the exciplex fluorescence was observed in dilute solutions of [VPh unit] = 3 × 10^{-4} M and [PhMMA unit] = 5 × 10^{-4} M, where the interpolymer interaction could be negligible, the exciplexes formed in the copolymers are considered to be intramolecular. In fact, in the case of poly(VPh-*co*-DMAMMA) there was no difference in the profile of the fluorescence spectra in the concentration range 10^{-4}–10^{-3} M VPh unit (data not shown).

The fluorescence quantum yields of the phenanthrene monomer fluorescence Φ_M and the exciplex fluorescence Φ_E, and the lifetimes of the exciplex fluorescence τ_E of four copolymers, are listed in Table II, and the characteristics of the copolymers are qualitatively summarized in Table III. From the Φ and τ data in Table II, these copolymers can be divided into three groups: i.e., poly(VPh-*co*-DMAS) has a low Φ_M, a high Φ_E, and a long τ_E; poly(VPh-*co*-DMAMMA) has a high Φ_M, a low Φ_E, and a long τ_E; and poly(PhMMA-*co*-DMAS) and poly(PhMMA-*co*-DMAMMA) have low Φ_M, low Φ_E, and short τ_E.

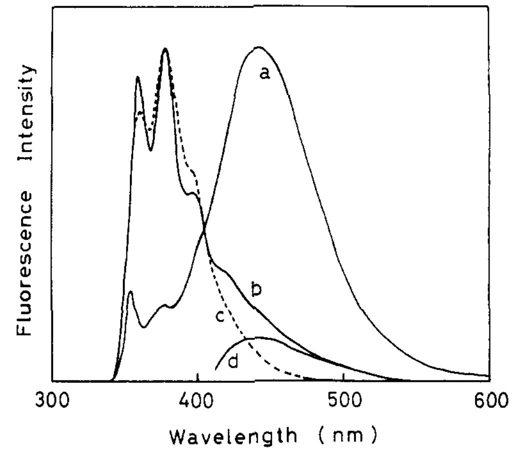


Figure 1. Fluorescence spectra of copolymers of VPh with DMAS and DMAMMA in dioxane: (a) poly(VPh-*co*-DMAS)(59), (b) poly(VPh-*co*-DMAMMA) (50), (c) poly(VPh), [VPh unit] = 3 × 10^{-4} M. Excitation at 352 nm. Spectrum d was obtained by subtracting c from b.

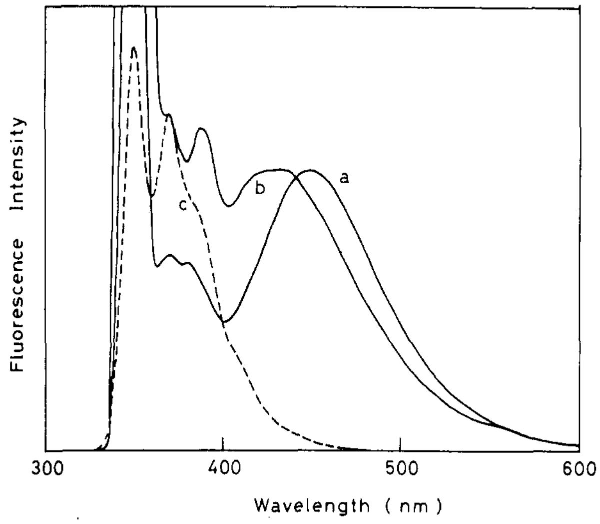
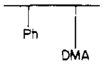
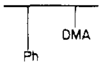
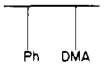


Figure 2. Fluorescence spectra of copolymers of PhMMA with DMAS and DMAMMA in dioxane: (a) poly(PhMMA-*co*-DMAS)(50), (b) poly(PhMMA-*co*-DMAMMA)(60), (c) poly(PhMMA), [PhMMA unit] = 5 × 10^{-4} M. Excitation at 348 nm.

Poly(VPh-*co*-DMAS) forms an intramolecular exciplex with a high Φ_E and a long τ_E easily because of its chemical structure satisfying the n = 3 rule and partly owing to energy migration among VPh units.[2] This intramolecular exciplex is considered to be formed from nearest-neighbor

Table III
Chemical Structure and Characteristics of Copolymer Systems

copolymer	structure	Φ_M	Φ_E	τ_E	possibility of exciplex formn[a]
poly(VPh-*co*-DMAS)	 Ph DMA	low	high	long	good
poly(VPh-*co*-DMAMMA)	 Ph DMA	high	low	long	poor
poly(PhMMA-*co*-DMAS)	 DMA Ph	low	low	short	none
poly(PhMMA-*co*-DMAMMA)	 Ph DMA	low	low	short	good

[a] The extent of overlap between phenanthrene and DMA chromophores in nearest neighbors judged from space-filling models.

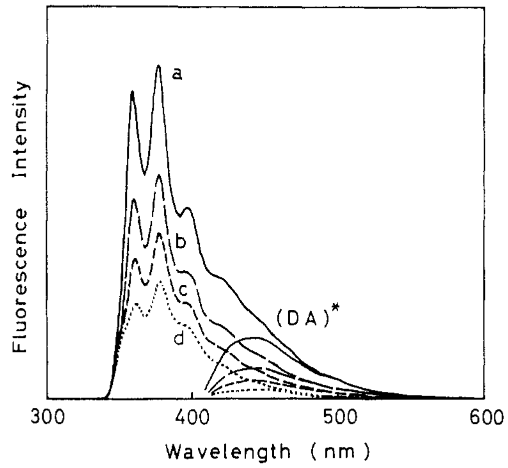


Figure 3. Fluorescence spectra of poly(VPh-*co*-DMAMMA) in dioxane: (a) poly(VPh-*co*-DMAMMA)(25), (b) poly(VPh-*co*-DMAMMA)(50), (c) poly(VPh-*co*-DMAMMA)(67), (d) poly(VPh-*co*-DMAMMA)(80), [VPh unit] = 3×10^{-4} M.

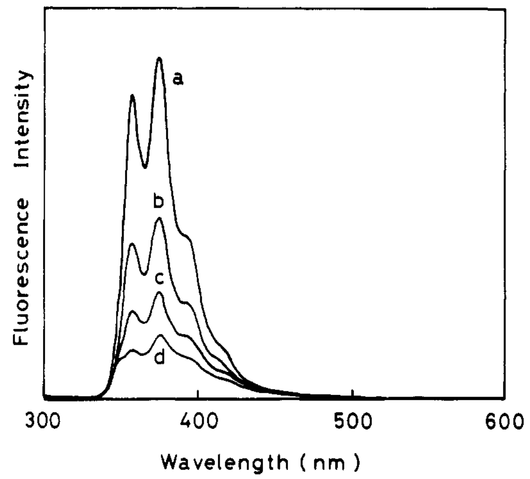


Figure 4. Fluorescence spectra of poly(VPh-*co*-MMA) in dioxane: VPh content of (a) 23, (b) 42, (c) 48, and (d) 60 mol %, [VPh unit] = 3×10^{-4} M. Excitation at 352 nm.

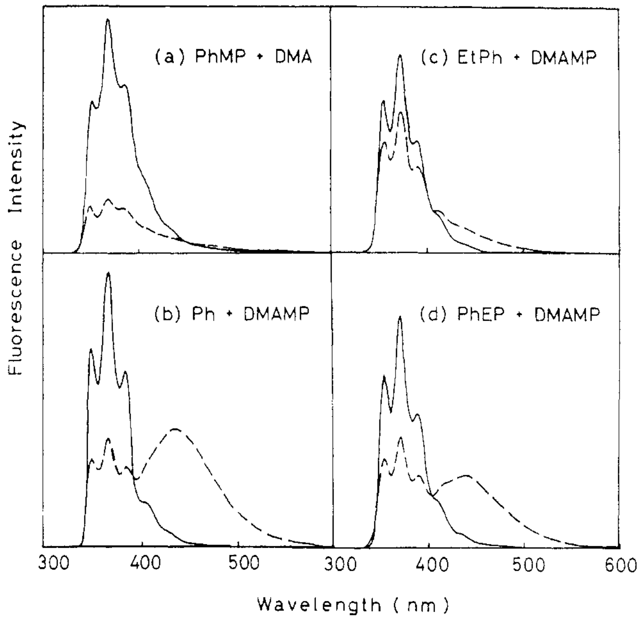


Figure 5. Fluorescence spectra of low-molecular-weight phenanthrene derivative + *N*,*N*-dimethylaniline derivative systems in dioxane: (a) PhMP + DMA, (b) Ph + DMAMP, (c) EtPh + DMAMP, (d) PhEP + DMAMP, [phenanthrene derivative] = (3-4) $\times 10^{-4}$ M, [DMA derivative] = 0 (—) and 2.5×10^{-2} (- -) M.

phenanthrene and DMA moieties. In fact, the emission properties and the oxidation potential of the exciplex are very similar to those of its bichromophoric model compound 1-[4-(dimethylamino)phenyl]-3-(9-phenanthryl)propane, phenanthryl-$(CH_2)_3$-DMA.[3,4]

Poly(VPh-*co*-DMAMMA) with a high Φ_M and a low Φ_E forms with difficulty an intramolecular exciplex with a long τ_E. The fluorescence spectra of poly(VPh-*co*-DMAMMA) with different monomer compositions at constant concentrations of VPh units are shown in Figure 3, where the fluorescence spectrum of the exciplex (DA)* was obtained by subtracting the poly(VPh) fluorescence spectrum part from each spectrum of poly(VPh-*co*-DMAMMA). Both the exciplex and the phenanthrene monomer fluorescence intensities decreased with decreasing DMAMMA content. To make the role of DMAMMA in the copolymer clear, this copolymer was compared with poly(VPh), poly(VPh-*co*-DMAS), and the copolymer of VPh and methyl methacrylate (MMA), poly(VPh-*co*-MMA), in which electronic energy migration could occur among phenanthrene groups. Quantum yields and lifetimes of the phenanthrene monomer fluorescence parts of poly(VPh), its dimer model compound 1,3-di-(9-phenanthryl)propane, and its monomer model compound EtPh increased in this order.[4] These changes could be attributable to the formation of intramolecular excimers between nearest-neighbor phenanthrene moieties, with low fluorescence quantum yield.[5] In the case of poly(VPh-*co*-MMA) the phenanthrene monomer fluorescence intensity increased with increasing MMA content because of decrease in excimer formation as shown in Figure 4. In this copolymer MMA units inhibit energy migration among VPh groups and suppress intramolecular excimer formation between nearest neighbors. On the other hand, in poly(VPh-*co*-DMAS) the exciplex fluorescence intensity was substantially constant independent of monomer composition in the range 23–75 mol % VPh.[2] In this copolymer, although DMAS units inhibit energy migration, formation of an intramolecular exciplex by rapid energy migration from an excited phenanthrene unit to an exciplex-forming site of nearest-neighbor phenanthrene and DMA moieties does occur. But in the case of poly(VPh-*co*-DMAMMA) the exciplex fluorescence intensity was not constant and decreased with decreasing DMAMMA content (Figure 3), and the phenanthrene monomer fluorescence intensity similarly decreased. In this copolymer DMAMMA units can inhibit energy migration but cannot act as efficient quenchers to form a nearest-neighbor intramolecular exciplex, presumably for steric reasons. The exciplex fluorescence intensity increased with increasing concentration of DMA as shown in Figure 3. Therefore, we conclude that the intramolecular exciplex observed in poly(VPh-*co*-DMAMMA) was formed from non-nearest-neighbor phenanthrene and DMA moieties.

In poly(PhMMA-*co*-DMAS) and poly(PhMMA-*co*-DMAMMA), Φ_M was considerably lower than that of the poly(PhMMA) (Table II). The values of Φ_M and τ_M of poly(PhMMA) were in turn similar to those of its model compound PhMP, showing negligible concentration quenching. From these results, it can be suggested that the excited phenanthrene group in the copolymers is quenched by a DMA group, resulting in formation of an exciplex of low Φ_E. In these two copolymers Φ_M, Φ_E, and τ_E were comparable. These findings indicate that considerable exciplex could be formed between non-nearest-neighbor phenanthrene and DMA chromophores.

The fluorescence behavior of PhMP + DMA (or DMAMP) systems, which correspond to the monomer model systems of these copolymers, is interesting. The

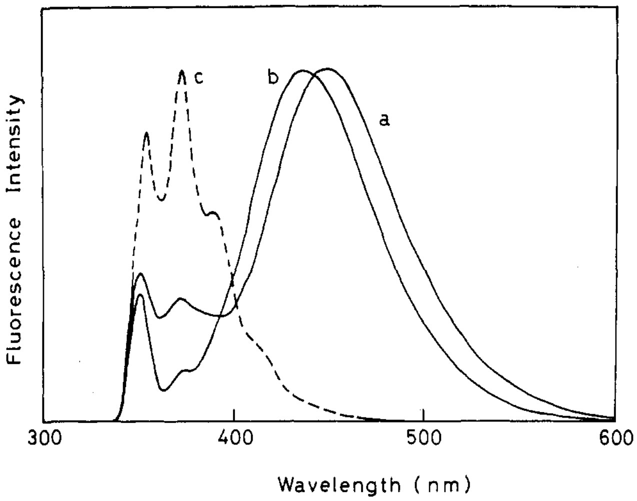


Figure 6. Fluorescence spectra of copolymers of PhEMA with DMAS and DMAMMA in dioxane: (a) poly(PhEMA-*co*-DMAS)(43), (b) poly(PhEMA-*co*-DMAMMA)(52), (c) poly(PhEMA), [PhEMA unit] = 4×10^{-4} M. Excitation at 350 nm.

Table IV
Amounts of DCB Anion Radical Measured by Flash Photolysis[a] and Relative Fluorescence Quantum Yields

	absorbance at 345 nm[b]				Φ_M
system	obsd	corn	cor	rel	$+ \Phi_E$
poly(VPh-*co*-DMAS)(59)	0.25_4	0.03_3	0.22_1	100	100
poly(VPh-*co*-DMAMMA)(50)	0.18_0	0.02_3	0.15_7	71	60
poly(PhMMA-*co*-DMAS)(25)	0.08_4	0.05_0	0.03_4	15	8[d]
poly(PhMMA-*co*-DMAMMA) (48)[c]	0.06_4	0.03_4	0.03_0	14	5[e]

[a] [phenanthrene unit] = 1.0×10^{-4} M, [DCB] = 6×10^{-2} M in DMF. [b] Part of the DCB anion radical was formed by electron transfer from the excited DMA unit to DCB. The amount was estimated from the results of flash photolysis of poly(DMAS) + DCB and poly(DMAMMA) + DCB systems. [c] [phenanthrene unit] = 1.3×10^{-4} M. [d] Poly(PhMMA-*co*-DMAS)(50). [e] Poly(PhMMA-*co*-DMAMMA)(60).

fluorescence of PhMP was quenched by DMA (Figure 5a) and DMAMP (not shown), forming exciplexes with low Φ_E and short τ_E, 11 and 10 ns, respectively. The fluorescence of phenanthrene was quenched by DMAMP (Figure 5b), yielding the strong exciplex fluorescence. The EtPh + DMAMP system showed the phenanthrene fluorescence quenching and an exciplex fluorescence (Figure 5c). It may be deduced, therefore, that the fluorescence of the exciplex depends on the chemical properties of substituent groups. We detected a strong exciplex fluorescence in the PhEP + DMAMP system as shown in Figure 5d. One can consider that the lowering of the exciplex fluorescence can result from the introduction of the carboxymethylene group ($COOCH_2$). The formation of exciplexes with low Φ_E and short τ_E in the copolymers could likewise be attributed to the carboxymethylene chain in the PhMMA unit as in the cases of PhMP systems.

Figure 6 shows the fluorescence spectra of poly(PhEMA), and its copolymers with DMAS and DMAMMA obtained by selective excitation of the PhEMA portion at 350 nm (λ_{max}). These copolymers, which have PhEMA instead of PhMMA as the phenanthrene-containing monomer, showed an intense and broad intramolecular exciplex fluorescence at ca. 440 nm together with a weak phenanthrene monomer fluorescence.

From the above results, it can be concluded that a structure satisfying the $n = 3$ rule is not always necessary for formation of an intramolecular exciplex and that considerable exciplex is formed between two chromophores when the phenanthrene moiety is linked to the main chain with a flexible group.

Electron Transfer to an Electron Acceptor, DCB. We have studied the intramolecular exciplex in the poly(vinylaromatics) from the standpoint of its application to conversion of light energy into chemical potential. The electron-donating ability of the intramolecular exciplex in poly(VPh-*co*-DMAS) is very close to that of the phenanthrene anion radical and larger than that of excited phenanthrene in polar media.[3] In poly(VPh-*co*-DMAS) + DCB systems, the DCB anion radical was generated by both electron transfer via exciplex and direct electron transfer from the excited phenanthrene unit.[2]

In the present four copolymer + DCB systems the amounts of the DCB anion radical generated in DMF were determined by measuring the intensity of the transient absorption band of the DCB anion radical at 345 nm 50 μs after flash and are listed in Table IV. The amounts of DCB anion radical detected in copolymers at constant concentration of phenanthrene units decreased in the order poly(VPh-*co*-DMAS) > poly(VPh-*co*-DMAMMA) > poly(PhMMA-*co*-DMAS) ≅ poly(PhMMA-*co*-DMAMMA). The order is the same as that of the overall fluorescence quantum yield of these copolymers in dioxane as shown in Table IV. In the PhMMA-containing copolymer systems the contribution of the exciplex to DCB anion radical formation could be smaller than that in the poly(VPh-*co*-DMAS) + DCB system because of radiationless deactivation processes caused by the carboxymethylene group, which decreased τ_E in these copolymers. As a result the amounts of DCB anion radical in these systems were small in comparison with the other systems.

Conclusion

Poly(VPh-*co*-DMAS) exhibits an intense intramolecular exciplex fluorescence, whereas poly(VPh-*co*-DMAMMA), poly(PhMMA-*co*-DMAS), and poly(PhMMA-*co*-DMAMMA) show only a weak exciplex fluorescence. Poly(VPh-*co*-DMAMMA) is considered to form with difficulty an intramolecular exciplex from non-nearest-neighbor phenanthrene and DMA moieties. In PhMMA-containing copolymers the excited phenanthrene portion is quenched effectively by a DMA group irrespective of its location, but the resulting exciplex has low Φ_E and short τ_E because of the attachment of the carboxymethylene chain to the phenanthrene moiety. The photoinduced electron transfer from copolymer to DCB is observed in all copolymer systems, and the amount of DCB anion radical detected is largest in the poly(VPh-*co*-DMAS) + DCB system.

References and Notes

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