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Photon-Harvesting Vinylphenanthrene–Methacrylic Acid Polymers: Triplet-State Migration and Trapping in Rigid Solution

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ABSTRACT: The delayed emission spectrum of the alternating copolymer of 9-vinylphenanthrene and methacrylic acid was compared with those of the corresponding random copolymers in rigid solution at 77 K. All fluorescence, phosphorescence, and delayed fluorescence spectra of poly(9-vinylphenanthrene) showed broad emission, indicating the presence of trap sites in both singlet and triplet states. On the other hand, the alternating copolymer has no trap sites in organic rigid solution, which permits long-distance triplet energy migration and thus efficient triplet–triplet annihilation. However, this is not the case in aqueous rigid solution; i.e., the alternating copolymer has deep traps. Intramolecular triplet energy transfer to the covalently bound anthracene groups was also enhanced by triplet energy migration in the alternating copolymer.

Introduction

It is well-known that singlet energy migration along polymer chains is terminated via excimer formation. A number of investigations have been carried out to clear up the effect of the polymer structure on such photophysical properties of aromatic vinyl polymers.[1] One interesting class of polymers is that of alternating polymers, which are expected to be superior candidates for "photon-harvesting" polymers because excimer formation would be essentially eliminated and energy transfer to traps would occur efficiently. In this context, we have been investigating the fluorescence properties of a series of amphiphilic alternating copolymers containing naphthalene[2,3] and phenanthrene[4,5] chromophores. Our previous results indicate an absence of excimer-forming sites in organic solution[2a,4] but not in water.[2b,3,4] However, significant singlet energy migration and transfer have been implicated in both solutions.[2-4] Consequently, we still do not have a clear model for understanding the relationship between polymer conformation and photophysical properties in solution.

These situations are expected to be similar for the triplet state. There are a few reports on triplet photophysics of alternating copolymers containing carbazole[6] and naphthalene[7,8] chromophores. Yokoyama et al.[6] demonstrated that triplet energy migration in the alternating copolymer of *N*-vinylcarbazole and fumaronitrile is appreciably slower than that in poly(*N*-vinylcarbazole). On the other hand, Fox et al.[7] reported that triplet migration in the alternating copolymer containing vinylnaphthalene or styrene groups is as efficient as that in the corresponding homopolymers. It has recently been reported for the alternating naphthalene copolymer that delayed fluorescence consists of both monomeric and excimeric components in a solid film but is monomeric in rigid solution.[8] Some of these differences in photophysical properties of polymers may be attributed to the nature of the chromophores. In fact, Ito et al.[9] recently demonstrated that the mechanism of triplet energy migration in polymer films is much different for carbazole and phenanthrene chromophores.

In the present work, we compare the triplet energy migration processes in alternating and random copolymers of 9-vinylphenanthrene and methacrylic acid in rigid solution at 77 K. Intramolecular energy transfer to the covalently bound anthracene groups is also examined.

Experimental Section

Materials. The alternating and random copolymers (a-MPh and r-MPh(*x*)) are those reported previously.[4] Anthracene-loaded copolymers (a-MPh–A and r-MPh(*x*)–A(*y*)) are also used.[4] Characterization of the polymer samples is shown in Table I.

2-Methyltetrahydrofuran (MTHF) was dried over sodium and distilled. *N*,*N*-Dimethylformamide (DMF) was dried over KOH and distilled. Water was deionized by passing through an ion-exchange resin column and distilled.

Measurements. The steady-state delayed emission spectra at 77 K were recorded on a Shimadzu RF-502A spectrofluorimeter with a phosphorescence attachment, including a cylindrical chopper operated at a frequency of 4 kHz. Polymer solutions in Pyrex tubes were outgassed by repeated freeze–pump–thaw cycles. Decays of delayed emission were traced on an oscilloscope. The lower limit of lifetime measurement was ca. 50 ms.

Results and Discussion

Emission Spectra in Organic Rigid Solution. Figure 1 shows the total emission spectra of the alternating and random copolymers at 77 K. The spectrum of poly(9-vinylphenanthrene) (PVPh) was slightly broadened compared with that of r-MPh(12). Furthermore, the fluorescence intensity tends to decrease with increasing phenanthrene (Phen) content in the copolymer.[10] Such phenomena have been previously observed at room temperature.[4] Itaya et al.[11] reported that there is little interaction between neighboring Phen groups in PVPh at 77 K. However, the present results suggest the self-quenching of the singlet state in PVPh even at 77 K. The spectral features of the alternating copolymer (a-MPh) were virtually identical with that of r-MPh(12), indicating the absence of self-quenching.

Phosphorescence from Phen chromophores also appeared in the longer wavelength region (>460 nm). Table II gives the intensity ratios of phosphorescence and fluorescence (I_P/I_F), which decrease with increasing Phen content in r-MPh. This suggests that the triplet state of

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Table I
Properties of Polymer Samples[a]

polym	copolym composn[b]		MW[c]
	Phen	Anth	
r-MPh(3)	0.03		2.1×10^5
r-MPh(12)	0.12		1.2×10^5
r-MPh(42)	0.42		3.9×10^4
PVPh	1.0		1.0×10^4
a-MPh	0.51		2.0×10^5
r-MPh(12)-A(1.0)	0.12	0.01	
r-MPh(99)-A(1.0)	0.99	0.01	
a-MPh-A(1.0)	0.51	0.01	

[a] Reference 4. [b] Mole fraction in the copolymer; Anth, anthracene. [c] Molecular weight determined by GPC.

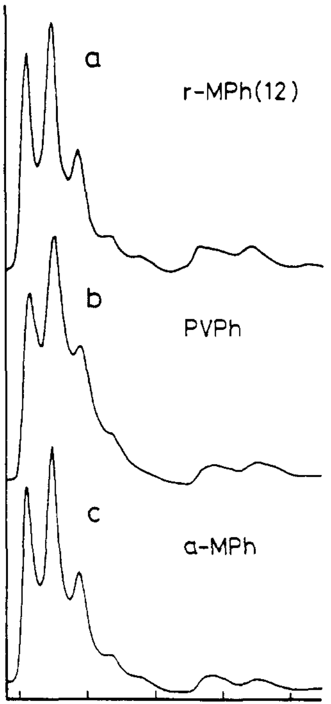

Figure 1. Total emission spectra of Phen polymers at 77 K: (a) r-MPh(12) in MTHF-DMF (8:2); (b) PVPh in MTHF; (c) a-MPh in MTHF. Excitation wavelength, 304 nm.

Table II
Ratios of Emission Intensities for Phen Polymers

polym	I_P/I_F[a]	I_{DF}/I_P[b]
r-MPh(3)[c]	0.18	<0.01
r-MPh(12)[d]	0.14	0.027
r-MPh(42)	0.14	0.053
PVPh	0.12	0.048
a-MPh	0.11	0.19

[a] Calculated from the total emission spectra (Figure 1). [b] Calculated from the delayed emission spectra (Figure 2). [c] Measured in DMF. [d] Measured in MTHF-DMF (8:2).

r-MPh with higher Phen content is quenched more effectively than the singlet state.[12] It is interesting to note that a-MPh has the lowest I_P/I_F value; i.e., the triplet state of a-MPh is largely quenched despite the absence of self-quenching of the singlet state. We ascribe this exclusively to efficient triplet-triplet (T-T) annihilation in a-MPh.

Figure 2 compares the delayed emission spectra for the copolymers. The phosphorescence spectrum of PVPh, which appeared above 460 nm, was slightly broadened and its emission intensity was decreased[10] just as the fluorescence spectrum was (Figure 1). We also found that the 0-0 band of phosphorescence of PVPh is red-shifted by ca. 10 nm compared with that of r-MPh(12). This is apparently due to the perturbation of the triplet energy by neighboring chromophores. Ito et al.[9b] reported that the phosphorescence spectra of poly[(9-phenanthrylmethyl methacrylate)-*co*-(methyl methacrylate)] films gradually shift to longer wavelength with increasing chromophore concentration. They referred this spectral shift to the stabilized state acting as a trap, as distinguished from the triplet excimer. It should be noted that the spectral shift is smaller for the present polymer system because of weak intermolecular chromophore interaction. The phosphorescence spectrum of a-MPh was similar to that of r-MPh(12) whereas the 0-0 band for the former was red-shifted by ca. 5 nm compared with that for the latter. However, since no observable shortening of the phosphorescence decay was observed for a-MPh, as will be seen later, this small spectral shift does not seem to be the result of a trap.

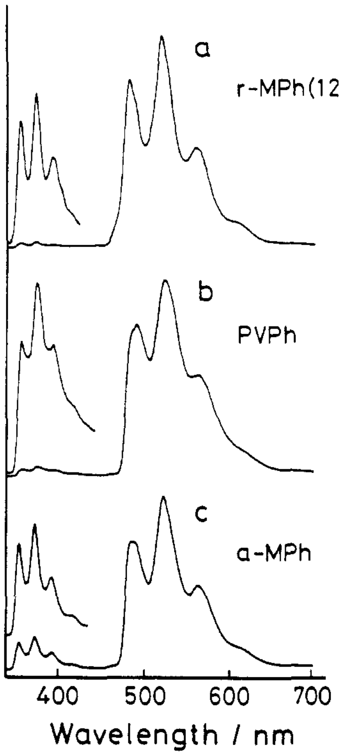

Figure 2. Delayed emission spectra of Phen polymers at 77 K: (a) r-MPh(12) in MTHF-DMF (8:2); (b) PVPh in MTHF; (c) a-MPh in MTHF. Excitation wavelength, 304 nm.

The delayed emission below 400 nm can be assigned to the delayed fluorescence resulting from T-T annihilation (Figure 2):

$$^3\text{Phen}^* + {}^3\text{Phen}^* \rightarrow {}^1\text{Phen}^* + \text{Phen} \quad (1)$$

This is further confirmed by the fact that the delayed fluorescence intensity (I_{DF}) of a-MPh increases accurately with the square of the phosphorescence intensity (I_P). The spectral features of delayed fluorescence were very similar to those of prompt fluorescence for each polymer. For example, the delayed fluorescence of PVPh is slightly broadened, indicating a weakly bound excimer-like emission that is not present in a-MPh. As shown in Figure 2, the relative intensities of phosphorescence and delayed fluorescence varied with Phen content in r-MPh. The ratios of I_{DF}/I_P are given in Table II. The values of I_{DF}/I_P initially increased with Phen content in r-MPh, whereas that of PVPh was decreased. A similar tendency has been reported for the I_{DF} values of naphthalene copolymers by Fox et al.[13] They suggested that the phosphorescence

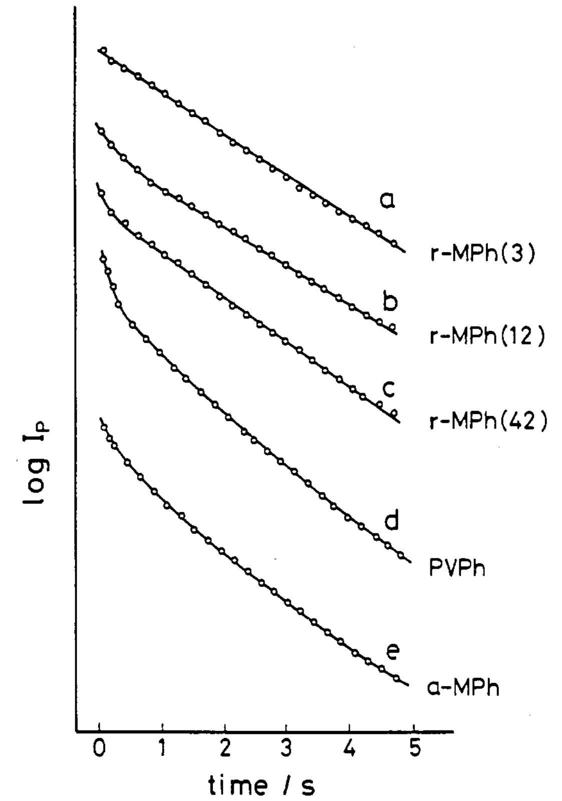

Figure 3. Phosphorescence decay curves of Phen polymers at 77 K: (a) r-MPh(3) in DMF; (b) r-MPh(12) in MTHF–DMF (8:2); (c) r-MPh(42) in MTHF; (d) PVPh in MTHF; (e) a-MPh in MTHF. Excitation wavelength, 304 nm; emission wavelength, 520 nm.

Table III
Lifetimes of Phosphorescence and Delayed Fluorescence in MTHF at 77 K[a]

	phosphorescence			delayed
polym	a_s	τ_s, s	τ_l, s	fluorescence:[b] τ_l, s
r-MPh(3)[c]			3.1	
r-MPh(12)[d]	0.29	0.48	3.6	0.32
r-MPh(42)	0.27	0.30	2.8	0.43
PVPh	0.60	0.31	2.5	<0.1
a-MPh	0.36	0.40	2.6	0.38

[a] Measured at a given light intensity. Excitation wavelength, 304 nm; emission wavelength, 520 nm (phosphorescence) and 370 nm (delayed fluorescence). The decay curves are analyzed by using the following equation: $I(t) = a_s \exp(-t/\tau_s) + (1 - a_s) \exp(-t/\tau_l)$. [b] The short-lifetime component decays too fast to be analyzed. [c] In DMF. [d] In MTHF–DMF (8:2).

Table IV
Excitation Light Intensity Dependence of Phosphorescence Lifetimes for PVPh and a-MPh in MTHF at 77 K

	PVPh			a-MPh		
relative I_P[a]	a_s	τ_s, s	τ_l, s	a_s	τ_s, s	τ_l, s
100	0.60	0.31	2.5	0.36	0.40	2.6
14	0.35	0.40	2.3	0.32	0.87	2.7
2	0.30	0.56	2.4	0.32	1.1	2.8
0.5	0.29	0.52	2.3	0.31	1.3	2.6

[a] Relative intensity of phosphorescence.

depletion process competes with the annihilation process in the long naphthalene segments, leading to the decreased delayed fluorescence intensity. However, this does not explain the lower I_{DF}/I_P value for PVPh. A possible explanation is that the quantum yield of delayed fluorescence of PVPh is decreased compared with that of r-MPh with low Phen content, as the lifetime is (see below). However, for a precise discussion it is necessary to take into account the strong dependence of I_{DF} and I_P on molecular weight of polymers.[14,15]

In contrast with PVPh, a-MPh has the highest I_{DF}/I_P value, indicating the efficient T–T annihilation (Table II). This remarkable feature seems to be common to alternating copolymers regardless of different phosphorescence properties.[6,7] Yokoyama et al.[6] reported that the phosphorescence of poly(*N*-vinylcarbazole) (PVCz) results almost entirely from traps, which do not participate in T–T annihilation because migrating triplets are immediately captured at trap sites, leading to a decrease in the delayed fluorescence intensity. On the other hand, a strong delayed fluorescence for the alternating copolymer of vinylcarbazole and fumaronitrile was observed. These workers showed that the phosphorescence of the alternating copolymer is emitted from both migrating and trapped triplets because of the slow rate of energy migration and that the migrating triplets primarily contribute to the T–T annihilation. Here it may be pointed out that there are very few trapping sites in alternating copolymer. In the preceding paper,[4] we indicated that a-MPh has the highest overall rate of fluorescence quenching in spite of the slow migration rate, primarily due to the absence of excimer-like traps. These facts strongly suggest that chromophore alternation decreases the number of trap sites per coil and enhances the long-distance triplet energy migration and T–T annihilation, even though it may decrease the migration rate. However, it should be still noted that there is a difference in molecular weight between a-MPh and r-MPhs (Table I), which affects the I_{DF}/I_P values. Such enhanced delayed fluorescence has also been observed for sterically hindered naphthalene polymers.[16]

The decay curves of phosphorescence for the polymers showed a noticeable deviation from simple exponential behavior except for r-MPh(3) (Figure 3). The lifetimes obtained from a two-exponential fit to the phosphorescence decays are listed in Table III. The lifetime of the long-lifetime component decreased with increasing Phen content in r-MPh, which is indicative of a self-quenching process as described above. It is reasonable to think that the short-lifetime component reflects the energy migration process including T–T annihilation and energy trapping. In order to distinguish these processes, we investigated the effect of the intensity of excitation light on the phosphorescence decays (Table IV). Decreasing the light intensity increased the lifetime of the short-lifetime component and decreased its fraction, while simultaneously eliminating the delayed fluorescence. However, a short-lifetime component remained for PVPh at the lowest light intensity that could be used. This clearly indicates the presence of trap sites in PVPh.[17] Furthermore, it appears that energy migration in PVPh continues over several hundred milliseconds,[18] which is longer than in PVCz.[6] Ito et al.[9] reported that the migration rate constant for the Phen polymer film is 1 order of magnitude smaller than that for the carbazole polymer film. They also demonstrated that the triplet energy migration in the former film occurs by a trapping–detrapping process at the trap sites, which is responsible for the slow migration rate. On the other hand, the decay curve for a-MPh at the lowest light intensity did not have such a short lifetime component as that for PVPh. This strongly suggests that there are essentially no trap sites in a-MPh and that mobile triplets exclusively contribute to T–T annihilation.

The delayed fluorescence decayed much faster relative to the phosphorescence for all polymers (Table III). Such a phenomenon has been observed for many aromatic polymers.[19] In particular, the lifetime for PVPh was too

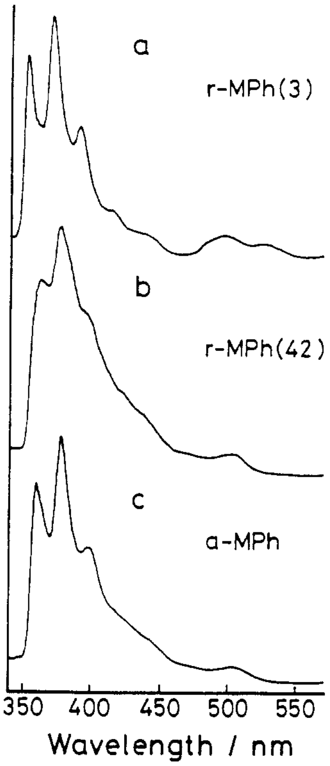

Figure 4. Total emission spectra of Phen polymers in aqueous solution (pH 9) at 77 K: (a) r-MPh(3); (b) r-MPh(42); (c) a-MPh. Excitation wavelength, 304 nm.

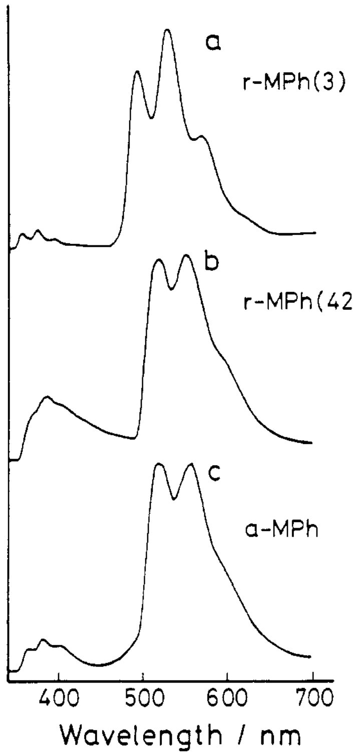

Figure 5. Delayed emission spectra of Phen polymers in aqueous solution (pH 9) at 77 K: (a) r-MPh(3); (b) r-MPh(42); (c) a-MPh. Excitation wavelength, 304 nm.

Table V
Lifetimes of Phosphorescence and Delayed Fluorescence in H_2O (pH 9) at 77 K

	phosphorescence			delayed
polym	a_s	τ_s, s	τ_l, s	fluorescence: τ_l, s
r-MPh(3)	0.42	0.20	2.2	<0.1[a]
r-MPh(42)			~0.1[a]	<0.1[a]
a-MPh			~0.1[a]	<0.1[a]

[a] The short-lifetime component decays too fast to be analyzed.

short to be analyzed. This may be explained by the fact that energy migration and thus T–T annihilation occur faster, shortening the lifetime of delayed fluorescence.

Emission Spectra in Aqueous Rigid Solution. Figure 4 shows the total emission spectra of the alternating and random copolymers in aqueous solution of pH 9 at 77 K. The spectrum of r-MPh(42) was broader and showed an excimer-like emission, a tendency that has been observed at room temperature.[4] We also found that for a-MPh there is a slight increase of the relative intensity in the longer wavelength region. These results suggest that for r-MPh(42) and a-MPh the preferred conformations for excimer formation are frozen in at 77 K.

Several interesting phenomena were observed in the delayed emission spectra (Figure 5). The spectrum of r-MPh(3) showed the normal Phen phosphorescence. However, the delayed fluorescence appeared in spite of small Phen content in the copolymer, suggesting that r-MPh(3) has the compact conformation in H_2O which allows the Phen groups to approach each other or that polymer aggregation has occurred. On the other hand, the spectral shape of phosphorescence for r-MPh(42) and a-MPh changed significantly and the 0–0 band was red-shifted by more than 20 nm. Furthermore, relatively stronger, broader, and red-shifted delayed fluorescence was observed. These observations clearly indicate that there are deep traps for r-MPh(42) and a-MPh, which might be called a "triplet state eximer", and that there are a number of excimer sites in the singlet state. It may be further said that the compact conformation in H_2O remarkably enhances the energy migration and thus T–T annihilation although it increases the self-quenching of the triplet state. The lifetimes of phosphorescence and delayed fluorescence for these polymers were too short to be determined (Table V). These results are qualitatively in agreement with those for sulfonated poly(2-vinylnaphthalene) reported by Guillet et al.[20] They proposed a "hypercoiled conformation" for these polymers in aqueous solution. We demonstrated in the preceding paper[4] that even for the alternating copolymer the compact conformation in H_2O leads to interaction of Phen groups and thus to remarkable self-quenching of fluorescence. The present results confirm this phenomenon and show that delayed emission spectra are more sensitive to such chromophore interactions.

Energy Transfer to Covalently Bound Anthracene Groups in Organic Rigid Solution. Figure 6 shows the total emission spectra of anthracene-loaded polymers in MTHF at 77 K excited at 304 nm. At this wavelength the Phen absorbs most of the light. The increase in the relative intensity of sensitized anthracene (Anth) fluorescence (>400 nm) with Phen loading implies that efficient energy transfer is occurring:

$$^1\text{Phen}^* + \text{Anth} \rightarrow \text{Phen} + {}^1\text{Anth}^* \qquad (2)$$

However, we could not determine the quantum efficiency of energy transfer because of the uncertainty in several parameters in 77 K MTHF glasses such as fluorescence quantum yield, relative OD at the excitation wavelength, etc.[4]

In contrast, there are much more distinct differences between these polymers in the delayed emission spectra, as shown in Figure 7. The spectra of r-MPh(99)–A(1.0) and a-MPh–A(1.0) contain the phosphorescence (650–750 nm) and delayed fluorescence (400–450 nm) from Anth moieties as well as from Phen moieties. In the present case, both singlet–singlet and triplet–triplet energy transfer can

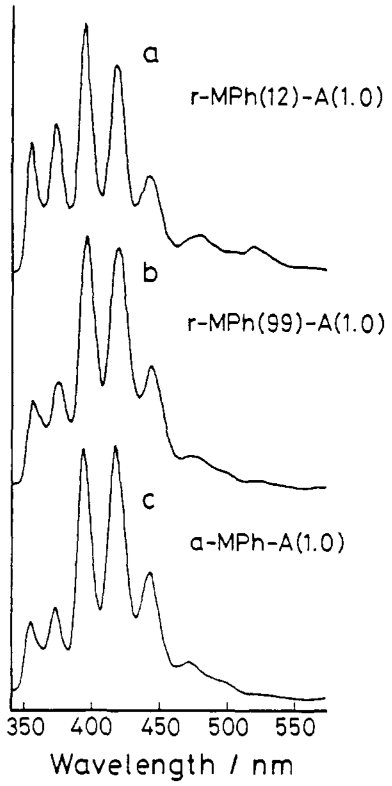

Figure 6. Total emission spectra of Anth-loaded polymers in MTHF at 77 K: (a) r-MPh(12)–A(1.0); (b) r-MPh(99)–A(1.0); (c) a-MPh–A(1.0). Excitation wavelength, 304 nm.

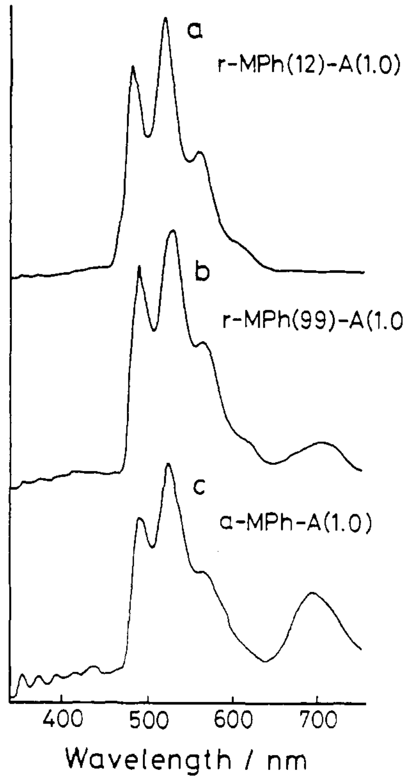

Figure 7. Delayed emission spectra of Anth-loaded polymers in MTHF at 77 K: (a) r-MPh(12)–A(1.0); (b) r-MPh(99)–A(1.0); (c) a-MPh–A(1.0). Excitation wavelength, 304 nm.

occur:

$$ {}^1\text{Phen}^* + \text{Anth} \rightarrow \text{Phen} + {}^1\text{Anth}^* \rightarrow {}^3\text{Anth}^* \tag{3} $$

$$ {}^1\text{Phen}^* \rightarrow {}^3\text{Phen}^* + \text{Anth} \rightarrow \text{Phen} + {}^3\text{Anth}^* \tag{4} $$

In the former case (eq 3), the sensitized Anth phosphorescence is emitted via intersystem crossing from the sensitized singlet state of Anth. In the latter case (eq 4), the formation of a Phen triplet is followed by T–T energy transfer to Anth. We believe that the latter process plays an important role in the formation of an Anth triplet because of the following:

(1) The quantum yield of triplet formation for Phen ($\Phi_{TM} > 0.8$) is larger than that for Anth ($\Phi_{TM} \sim 0.5$).[21] In fact, the direct excitation of Anth moiety in the copolymer or 9-anthracenemethanol resulted in quite weak phosphorescence.

(2) The decay curves of Phen phosphorescence for all polymers have a rapidly decaying component, which is too fast to be resolved with our equipment. This observation is indicative of T–T energy transfer from Phen to Anth. In addition, the relatively large increase of the sensitized Anth phosphorescence in the Anth-loaded alternating copolymer suggests that efficient migration of Phen triplets enhances the triplet energy transfer. This is supported by the fact that the long-lifetime component for a-MPh–A(1.0) ($\tau_l \sim 2.2$ s) is slightly decreased compared to that for a-MPh ($\tau_l = 2.5$ s) or r-MPh(3) ($\tau_l = 3.1$ s). It is noted that the most intense Anth delayed fluorescence occurs for a-MPh–A(1.0). This may be explicable in terms of efficient T–T annihilation followed by singlet–singlet energy transfer for the alternating copolymer:

$$ {}^3\text{Phen}^* + {}^3\text{Phen}^* \rightarrow {}^1\text{Phen}^* + \text{Anth} \rightarrow \text{Phen} + {}^1\text{Anth}^* \tag{5} $$

In addition, it is reasonable to elaborate on the mechanism of "heterogeneous" annihilation between the triplet states of Phen and Anth:

$$ {}^3\text{Phen}^* + {}^3\text{Anth}^* \rightarrow \left\{ \begin{array}{l} {}^1\text{Phen}^* + \text{Anth} \rightarrow \text{Phen} + {}^1\text{Anth}^* \\ \text{Phen} + {}^1\text{Anth}^* \end{array} \right. \tag{6} $$

However, it is difficult to determine which mechanism predominates without further experimental evidences; this remains a future subject of study.

Conclusion

The alternating copolymer a-MPh has no trap sites in the triplet state in organic rigid solution, permitting triplet energy migration along the long Phen sequences, thus facilitating T–T annihilation and intramolecular transfer to Anth traps for a-MPh–A(1.0). These triplet-state properties of a-MPh mirror the singlet-state properties.[4] Considering the fact that a single-step T–T energy transfer is unlikely to occur beyond a distance of 1.5 nm and that this transfer rate is relatively slow compared with that of the singlet state, these types of polymers with a long lifetime of phosphorescence and no trap sites are expected to be superior candidates for "triplet-energy-harvesting polymers". However, it should be noted that elimination of an interaction between neighboring chromophores is not sufficient to ensure efficient photon-harvesting polymers in more condensed chromophore systems such as in films and in aqueous media. Triplet-state photophysical studies on the present polymers in fluid solution and in films are now in progress and will be reported in a future paper.

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Registry No. a-MPh, 129894-82-2; r-MPh, 83714-23-2; PVPh, 86885-30-5.