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ALTERNATING COPOLYMERS CONTAINING AN AROMATIC CHROMOPHORE IN EVERY MONOMER UNIT. 2. EXCIMER FORMATION AND INTRAMOLECULAR ENERGY MIGRATION IN ALTERNATING COPOLYMERS OF NAPHTHYLALKYL METHACRYLATE AND VINYLNAPHTHALENE

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ALTERNATING COPOLYMERS CONTAINING AN AROMATIC CHROMOPHORE IN EVERY MONOMER UNIT. 2. EXCIMER FORMATION AND INTRAMOLECULAR ENERGY MIGRATION IN ALTERNATING COPOLYMERS OF NAPHTHYLALKYL METHACRYLATE AND VINYLNAPHTHALENE

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Key Words: Alternating Polymer, Naphthalene, Excimer, Energy Migration, Fluorescence Quenching

ABSTRACT

A series of alternating and random copolymers of 2-naphthylalkyl methacrylates (NpMMA and NpEMA) and 2-vinylnaphthalene (VNp) were synthesized, and their fluorescence properties in tetrahydrofuran (THF) were compared. All of the alternating

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copolymers containing NpMMA or NpEMA showed a weak excimer emission, indicating that excimer formation between naphthyl (Np) chromophores in the alternating methacrylate sequences cannot be perfectly inhibited. No distinct difference in the fluorescence from the NpMMA and VNp moieties in poly(NpMMA-alt-VNp) (a-NpVNp) suggests that practically the same chromophores are aligned along the whole polymer chain. This observation is sharp in contrast with the corresponding phenyl polymers exhibiting different spectral features. Fluorescence quenching studies, however, showed no enhancement of the quenching efficiencies for a-NpVNp among the present polymers. Therefore, energy migration between the nearest-neighboring Np chromophores would inefficiently occur, though this polymer has the highest density of chromophores.

INTRODUCTION

In recent years, polymers with multiple sensitizers became particularly attractive as light-harvesting polymers which can collect and convert light energy to a useful chemical one as in the case of photosynthetic systems [1, 2]. We have been investigating emission properties of various types of alternating copolymers containing aromatic chromophores which are expected to inhibit excimer formation and other excited-state quenching processes and thus, to facilitate energy migration [3-5]. At the present stage, however, the effect of chromophore alternation on the migration is unexpectedly small: alternating copolymers permit the singlet-state and triplet-state energy migration more efficiently than the corresponding random copolymer,s but less than the copolymers with higher chromophore contents. This result may be due in part to the insufficient density of chromophores in a polymer chain.

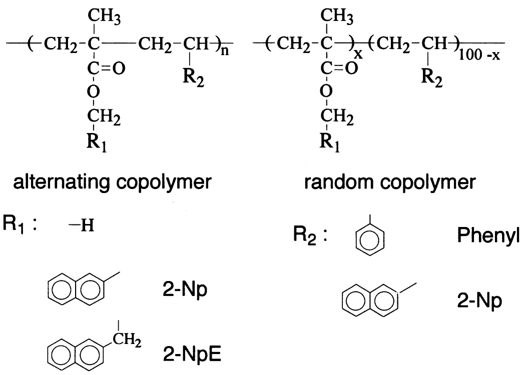
In this context, we have synthesized a new type of alternating copolymers with chromophores in the higher density. In the preceding paper, fluorescence properties of alternating copolymer containing a phenyl chromophore in each monomer unit, poly(benzyl methacrylate-*alt*-styrene), were examined [6]. The results obtained are follows: (1) it shows no excimer emission. (2) the phenyl chromophores in the methacrylate and styrene units have slightly different excited-state properties. (3) the fluorescence quenching study suggests no facilitation of energy migration. However, there is still room for concluding that these features are common to this type of alternating copolymers, because phenyl chromophores form an excimer inefficiently and have an intrinsically low migration efficiency as expected from the short Frster radius for self-transfer (ca. 0.65 nm) [7].

It is known that many polymers with naphthyl (Np) groups exhibit excimer formation and energy migration [8] and that Np chromophores have a longer Förster radius for self-transfer (ca. 1.2 nm) [9]. These features will allow us to check whether the above phenomena are general in the present type of alternating copolymers. In this paper, Np-containing polymers, poly(2-naph-thylmethyl methacrylate-alt-2-vinylnaphthalene) (a-NpVNp) and poly(2-(2-naphthyl)ethyl methacrylate-*alt*-2-vinylnaphthalene) (a-NpEVNp), are prepared and their fluorescence properties are compared with those for the prototype of alternating and random copolymers (Figure 1 where x represents the methacrylate content in the random copolymer in mol%).

EXPERIMENTAL

Materials

2-Naphthylmethyl methacrylate (NpMMA) and 2-(2-naphthyl)ethyl methacrylate (NpEMA) were synthesized according to the literature [10]. 2-Vinylnaphthalene (VNp) (from Aldrich) was purified by silica-gel column chro-



R_1	R_2	Alternating	Random
2-Np	Phenyl		**r-NpSt(x)**
H	2-Np	**a-MVNp**	**r-MVNp(x)**
2-Np	2-Np	**a-NpVNp**	**r-NpVNp(x)**
2-NpE	Phenyl	**a-NpESt**	**r-NpESt(x)**
2-NpE	2-Np	**a-NpEVNp**	**r-NpEVNp(x)**

Figure 1. Chemical structures of alternating and random copolymers: x represents the methacrylate content in the random copolymer in mol%.

matography with *n*-hexane as an eluent. Styrene (St) and methyl methacrylate (MMA) (from Wako Chemical) were distilled under reduced pressure before use.

Alternating and random copolymers were prepared as reported previously [5]. The compositions and molecular weights of copolymers were estimated according to the methods similar to those reported previously [6]. These data for alternating copolymers are listed in Table 1. The molecular weights of random copolymers were dependent on the composition of comonomer units: r-NpSt(x), $1.8\text{-}14 \times 10^4$; r-MVNp(x), $2.7\text{-}7.0 \times 10^4$; r-NpVNp(x), $2.7\text{-}9.5 \times 10^4$.

Measurements

Measurements of steady-state fluorescence spectra and fluorescence lifetimes were carried out for deaerated samples in THF, as reported previously [5].

RESULTS AND DISCUSSION

Alternating Polymerizations

Based on the previous results of alternating polymerization of MMA and VNp [11], alternating polymerizations were performed under a restricted condition: 0.67 of the methacrylate mole fraction in the feed; polymerization temperature, -20°C (Table 1). Since this type of polymerization can produce complete-

TABLE 1. Alternating Polymerization of Methacrylates (M_1) and Vinyl Aromatics (M_2)[a]

Polymer	M_1	M_2	Polym. time h	Yield %	M_1 in polymer[b] mol%	MW[c]
a-MVNp	MMA	VNp	5	40	52	1.2×10^5
a-NpVNp	NpMMA	VNp	5	23	47	1.4×10^6
a-NpESt	NpEMA	St	2.5	17	47	4.6×10^4
a-NpEVNp	NpEMA	VNp	5	53	54	1.6×10^5

[a] [EASC] / [methacrylate] = 0.6; $[M_1] / [M_2] = 2$; in toluene; polymerization temperature, -20 °C.

[b] Determined from absorption spectra.

[c] Polystyrene equivalent number-average molecular weight determined by GPC.

ly alternating copolymers [3, 5, 12], it is assumed that the present copolymers have only an alternating sequence, or negligible amount of defects, in the polymer chain. The highly alternating tendency in these polymers may also be supported, though indirectly, by the observation of no or extremely diminished excimer emission, as willl be shown below. Alternating polymerization of NpMMA and St was attempted many times under different conditions (e.g., the methacrylate mole fraction in the feed, 0.33-0.67; polymerization temperature, -30-0°C; polymerization time, 5-10 hours, etc.), but failed We have no clear reason for this.

Fluorescence Spectroscopy

In Figure 2, fluorescence spectra of three types of random copolymers containing ca. 50 mol% of Np chromophores are compared in THF. For r-NpSt(46), an excimer fluorescence emitted around 390 nm, together with a monomer fluorescence at ca. 340 nm. On the other hand, r-MVNp(42) showed a slightly red-shifted excimer fluorescence at 395 nm as well as a decreased monomer emission. The similar monomer emissions are suggestive of the Np chromophores in the NpMMA and VNp units being identical. This may be supported by the fact that the relative fluorescence intensities of r-NpSt(4) and r-MVNp(98), showing only a monomer emission, are very close (Figure 3). The stronger and red-shifted excimer emission for r-MVNp(42) clearly indicates the

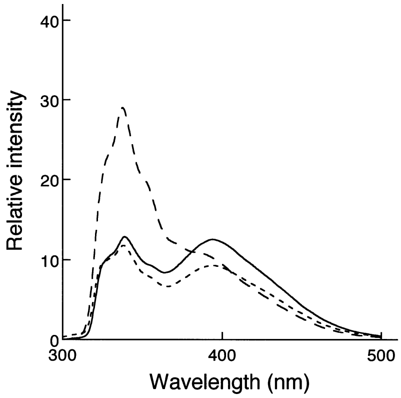


Figure 2. Fluorescence spectra of random copolymers containing Np chromophores in THF: ——— r-NpVNp(45); — — —, r-NpSt(46); – – –, r-MVNp(42); [Np]residue = 5×10^{-5} M; excitation wavelength, 281 nm; the peak intensities are normalized to that (100) of IPNp.

easiness of excimer formation in the VNp polymers. The spectrum of r-NpVNp(45) was found to be similar to that of r-MVNp(42), while the excimer emission slightly increased (Figure 2). Thus excimer would be formed in r-NpVNp(x) as freely as in r-MVNp(x).

In Figure 3, relative peak intensities for monomer emission (I_M), normalized to that of 2-isopropylnaphthalene (IPNp), are plotted as a function of x (the methacrylate content in mol%) in the copolymer. The I_M values of r-NpSt(x) decreased and those of r-MVNp(x) increased with increasing x (i.e., increasing the Np content), both of which are due to excimer formation. The values for r-NpVNp(x) were close to those for the above polymers with the corresponding x. This indicates that in this polymer excimer is formed mainly between the mutual NpMMA groups in the NpMMA-rich sequences and between the VNp groups in the VNp-rich sequences. Namely, the contribution of the excimer formed between the NpMMA and VNp groups to the fluorescence seems not to be large.

Figure 4 shows the fluorescence spectra of alternating copolymers. As reported previously [13, 14], a-MVNp exhibited no discernible excimer fluorescence. We confirmed that the fluorescence decayed exponentially (Table 2). On the other hand, a slightly decreased fluorescence with an increased tailing was observed for a-NpVNp. The fact that the excitation spectra of a-NpVNp recorded at different wavelengths are practically identical with the absorption spectrum may exclude the possibilities of formation of a ground-state dimer or aggregate

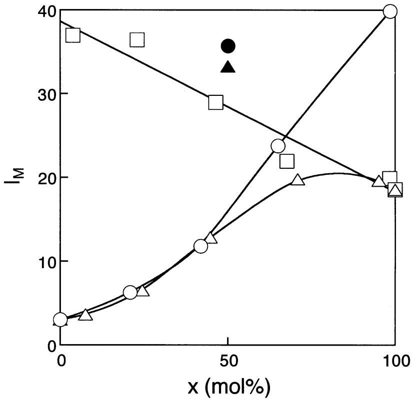


Figure 3. Relative intensities for monomer emission (IM) as a function of x: (○) r-MVNp; (△) r-NpVNp(x); (□) r-NpSt(x); (●) a-MVNp; (▲) a-NpVNp; the I_M values are normalized to that (100) of IPNp.

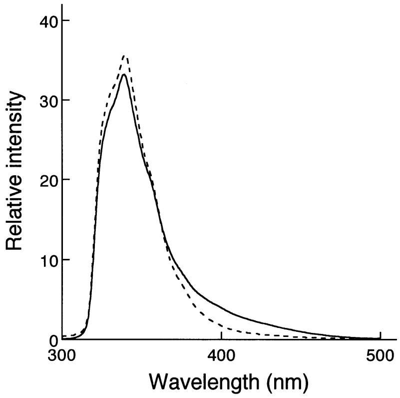


Figure 4. Fluorescence spectra of alternating copolymers containing Np chromophores in THF: ———, a-NpVNp; – – –, a-MVNp; [Np]residue = 5×10^{-5} M; excitation wavelength, 281 nm; the peak intensities are normalized to that (100) of IPNp.

TABLE 2. Fluorescence Decay Paramters for Alternating Np Polymers in THF[a]

Polymer	λ[b] nm	Species[c]	τ_i / a_i ns	
a-MVNp	330	M	51.3 / 1.00	
	440	E	-	
a-NpVNp	330	M	49.9 / 0.88	11.2 / 0.12
	440	E	54.0 / 1.71	4.4 / -0.71
a-NpESt	330	M	56.6 / 0.93	15.8 / 0.07
	440	E	54.5 / 2.35	2.5 / -1.35
a-NpEVNp	330	M	52.0 / 0.86	14.8 / 0.14
	440	E	54.7 / 6.21	2.0 / -5.21

[a] Decay curves are analyzed by using the equation: $I(t)=\Sigma a_i \exp(-t/\tau_i)$; Excitation wavelength, 280 nm.

[b] Emission wavelength.

[c] M, monomer; E, excimer.

of chromophores and contamination of fluorescent impurities. Therefore, we assigned the emission in the longer-wavelength region to an excimer fluorescence. The lifetime measurements supported the excimer formation in this polymer: the fluorescence monitored at 330 nm decayed nonexponentially and the decay curve monitored at 440 nm had a rising component ($\tau = 4$ ns). It can thus be concluded that excimer formation in the present type of polymers is not inhibited perfectly. Since no excimer emission is observed for a-MVNp, the contribution of the excimer formed between the VNp groups to the emission of a-NpVNp is negligible. Then, we consider the two possibilities: excimer is formed (1) between the nearest-neighboring Np groups in the successive NpMMA and VNp units, and (2) between the Np groups in the alternating NpMMA sequences. In a separate experiment, we found that poly(1-naphthylmethyl methacrylate-*alt*-St) emitted an excimer fluorescence as strongly as the corresponding random copolymer, indicating that excimer can be formed easily between the Np groups in the alternating methacrylate sequences [15]. It may be thus said that excimer formation between the alternating NpMMA sequences can occur, though we have no result for poly(NpMMA-alt-St). Further-more, taking into account the result of r-NpVNp(x) described above, the tailed emission in the longer-wavelength region observed for a-NpVNp seems to be assigned mainly to the excimer formed between the NpMMA sequences.

Nakahira *et al.* [10] demonstrated for poly(naphthylalkyl methacrylate)s that introduction of a polymethylene spacer between the polymer chain and the Np chromophore markedly suppresses excimer formation. To clarify the effect of the polymethylene length on excimer formation in the present type of polymers, fluorescence properties of the NpEMA-containing copolymers were examined (Figure 1). As expected, a-NpEVNp as well as a-NpESt showed a monomer fluorescence with a remarkably diminished tailing, as in the case of a-MVNp (Figure 5). However, some contribution of the excimer to the fluorescence was evidenced by their nonexponential fluorescence decay (Table 2). It is unexpected that a slight difference in the shape of monomer emission was observed for these polymers and that the fluorescence intensities of the NpEMA polymers were higher than those of the VNp polymers (Figure 5). These facts mean that the Np groups in the NpEMA and VNp sequences in a-NpEVNp are different chromophores, which is in contrast with the result for a-NpVNp that the Np groups in the NpMMA and VNp sequences are practically identical. We have no explanation for this discrepancy.

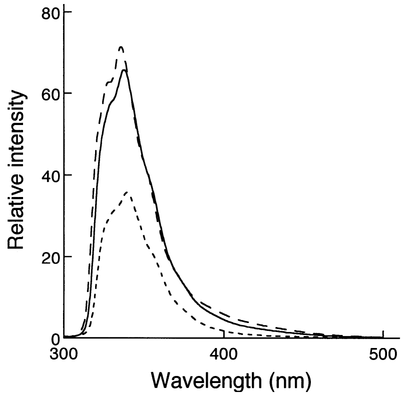


Figure 5. Fluorescence spectra of alternating copolymers containing NpEMA groups in THF: ———, a-NpEVNp; — — —, a-NpESt; – – –, a-MVNp; [Np]residue = 5×10^{-5} M; excitation wavelength, 281 nm; the peak intensities are normalized to that (100) of IPNp.

Fluorescence Quenching

In the same manner as reported previously [6], fluorescence quenching of the alternating copolymers and the model copolymers with a low Np content by carbon tetrachloride was examined. The values of weighted average lifetime (<τ>), Stern-Volmer constant (KSV), and second-order quenching rate constant (k_q) are listed in Table 3. Since the <τ> values were not largely different, the KSV and k_q values showed a similar tendency. The quenching for the alternating copolymers was always facilitated compared with that for the corresponding model copolymers, but the quenching efficiencies for a-NpVNp and a-NpEVNp were practically the same as that for a-MVNp.

These facts suggest that the increased density, or the decreased separation, of the Np chromophores in the former polymers does not contribute to the facilitation of energy migration. The Förster radii of self-transfer for 2-naphthalene compounds are reported to be around 1.2 nm [9], as described above. This value might not be far beyond the separation of nearest-neighboring Np groups even for a-NpVNp, leading to no facilitation of the energy migration during the excited singlet-state lifetime: molecular models showed that the distances for a-NpVNp (ca. 0.4-1.1 nm) and for a-NpEVNp (ca. 0.4-1.2 nm) were slightly shorter than 1.2 nm. In this connection, our preliminary experiment suggests that

TABLE 3. Fluorescence Quenching for Np Polymers in THF[a]

	NpMMA-polymer			NpEMA-polymer		
Type of polymer	$<\tau>$ ns	K_{SV} M^{-1}	k_q $M^{-1}s^{-1}$	$<\tau>$ ns	K_{SV} M^{-1}	k_q $M^{-1}s^{-1}$
r-NpSt(<5)	43.9	57	$1.3x10^9$	52.7	108	$2.1x10^9$
a-NpSt		(52)[b]		55.8	126	$2.3x10^9$
a-NpVNp	48.8	101	$2.1x10^9$	50.4	107	$2.1x10^9$
a-MVNp	51.3	101	$2.0x10^9$	51.3	101	$2.0x10^9$
r-MVNp(>95)	52.8	95	$1.8x10^9$	52.8	95	$1.8x10^9$

[a] Quencher, CCl_4.

[b] Data for r-NpSt(46).

triplet-state energy migration in a-NpVNp, which occurs in a long-time region (>ms), is rather efficient compared with that in a-NpSt and a-MVNp [15]. Another possibility is that the nearest-neighboring Np groups are different chromophores, diminishing the intrinsic migration efficiency itself. This is the case for poly(1-naphthylmethyl methacrylate-*alt*-1-vinylnaphthalene) [15]. From these results, we imagine that one kind of chromophores with a much larger Förster radius or a longer excited-state lifetime are required to be aligned along the polymer chain in the present type of alternating copolymers. Further studies are in progress along this line.

CONCLUSION

Excimer formation was found not to be inhibited perfectly in a-NpVNp. Furthermore, the fluorescence quenching for this polymer was not facilitated compared with that of the prototype of alternating copolymer (a-MVNp). The results imply that, to achieve an efficient energy migration in the present type of polymers, there should be several requirements other than the increased density of chromophores; e.g., identity of all chromophores loaded, selection of chromophores with a much larger Förster radius or a longer excited-state lifetime, etc.

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