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Alternating copolymers containing an aromatic chromophore in every monomer unit 3. Intramolecular excimer formation and energy transfer in poly(1-naphthylmethyl methacrylate-*alt*-2-vinylnaphthalene)

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Abstract

Alternating and random copolymers of 1-naphthylmethyl methacrylates (1NpMMA) and/or 2-vinylnaphthalene (VNp) were synthesized, and their fluorescence properties compared in tetrahydrofuran (THF) or 1,4-dioxane. The alternating copolymer of 1NpMMA and styrene (a-1NpSt) was found to form an excimer as freely as the corresponding random copolymer, and poly(1NpMMA-*alt*-VNp) (a-1NpVNp) also showed an excimer emission, indicating that excimer formation between the naphthyl (Np) chromophores in the alternating methacrylate sequences cannot be inhibited. The observation of monomer emission for 1NpVNp-type copolymers suggests that energy transfer occurs favourably from the 1NpMMA units to the VNp ones at room temperature, and that the transfer in the opposite direction, i.e., the transfer from the VNp units to the 1NpMMA ones, is possible at higher temperatures. The fluorescence-quenching study, however, showed no enhancement of the quenching efficiency for a-1NpVNp at room temperature. The predominant one-way energy transfer might not facilitate the long-range energy migration along the polymer chain.

Keywords: Alternating polymer; Naphthalene; Excimer; Energy migration; Fluorescence quenching

1. Introduction

As part of our continuing interest in the design of 'light-harvesting' polymers [1], we have recently investigated the fluorescence properties of alternating copolymers containing a phenyl or 2-naphthyl (2-Np) chromophore in each monomer unit [2,3]. The results showed that excimer formation was inhibited in the phenyl polymer, but not perfectly in the 2-Np polymer. The excimer emission observed for the latter polymer, however, has not been identified satisfactorily. Further, the fluorescence-quenching study indicated no enhancement of the quenching efficiency for both polymers. Contrary to our expectation [2,3], this result might lead to the conclusion that the increased density of chromophores in a polymer chain does not contribute to the facilitation of energy migration.

In this work, an investigation is undertaken to determine whether energy transfer or migration between the nearest-neighbouring chromophores occurs or not. We note here that there is little difference in the fluorescence emitted from the methacrylate and vinyl aromatic units in the above mentioned polymers [2,3]. This similarity will be favourable for efficient energy migration, but will make it difficult for us to investigate the

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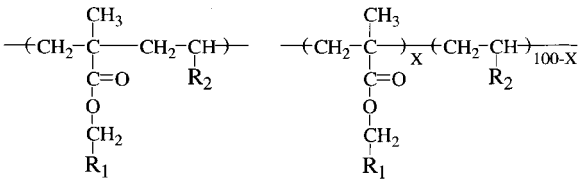
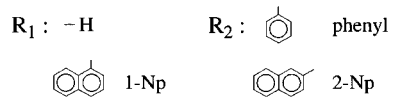


Alternating Copolymer Random Copolymer



R_1	R_2	Alternating	Random
H	2-Np	**a-MVNp**	**r-MVNp(x)**
1-Np	phenyl	**a-1NpSt**	**r-1NpSt(x)**
1-Np	2-Np	**a-1NpVNp**	**r-1NpVNp(x)**

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

migration process. Based on the fact that 1-Np and 2-Np chromophores exhibit a slightly different monomer and excimer fluorescence [4], here we synthesized alternating and random copolymers of 1-naphthylmethyl methacrylates (1NpMMA) and/or 2-vinylnaphthalene (VNp) (Fig. 1) and compared their fluorescence properties.

2. Experimental

1NpMMA was synthesized according to the literature [5] and purified by silica-gel column chromatography with *n*-hexane as an eluent. Other monomers were purified as reported previously [3].

Syntheses and characterizations of alternating and random copolymers were performed as reported previously [6]. Typical results of alternating polymerizations are listed in Table 1. As in our previous results [2,3,6,7], satisfactory copolymers with a moderate molecular weight were obtained under limited conditions. The molecular weights of random copolymers were determined by GPC: r-MVNp(x), 2.7–7.0 × 10^4; r-1NpSt(x), 2.2–13 × 10^4; r-1NpVNp(x), 3.5–13 × 10^4.

Steady-state fluorescence spectra and fluorescence lifetimes were measured for deaerated samples in tetrahydrofuran (THF) or 1,4-dioxane, as reported previously [6]. Fluorescence intensities were normalized to that of 2-isopropylnaphthalene (IPNp).

3. Results and discussion

3.1. Fluorescence spectroscopy at room temperature

In Fig. 2, fluorescence spectra of alternating and random copolymers are compared in THF. As reported previously [3], r-MVNp(x) showed an excimer fluorescence at the maximum of 395 nm, whereas a-MVNp showed only a monomer emission at ≈340 nm (Fig. 2(a)). For r-1NpSt(x), a slightly blue-shifted excimer emission around 390 nm and a structured monomer one around 340 nm were observed (Fig. 2(b)). The differences in the spectral shape and intensity of the monomer emission for the corresponding r-MVNp(x) and r-1NpSt(x) confirm that the Np chromophores in the VNp and 1NpMMA units are not the same. This is in contrast with the previous result that the copolymers of 2-naphthylmethyl methacrylate and VNp (a-NpVNp and r-NpVNp(x)) have similarity in the monomer emission [3].

It should be noted that a-1NpSt exhibited an excimer emission whose intensity was as high as that for the corresponding random copolymer, r-1NpSt(47). This clearly indicates that Np groups in the alternating 1NpMMA sequences can form an excimer easily. The same emission behaviour for a-1NpSt and r-1NpSt(47) was also observed by the fluorescence lifetime measurements. The fluorescence decays were described reasonably, though conveniently, by a double-exponential

Table 1
Alternating polymerization of methacrylates (M_1) and vinyl aromatics (M_2)[a]

Polymer	M_1	M_2	Yield (%)	M_1 fraction in polymer[b]	MW[c]
a-MVNp	MMA	VNp	40	0.52	1.2×10^5
a-1NpSt	1NpMMA	St	31	0.53	2.2×10^5
a-1NpVNp	1NpMMA	VNp	29	0.44	3.3×10^5

[a] [EASC]/[methacrylate] = 0.6; $[M_1]/[M_2] = 2$ in toluene; polymerization temperature, −20°C; polymerization time, 5 h; EASC, ethylaluminum sesquichloride.
[b] Determined from absorption spectra in THF using the corresponding homopolymers as standards.
[c] Polystyrene equivalent number–average molecular weight determined by GPC.

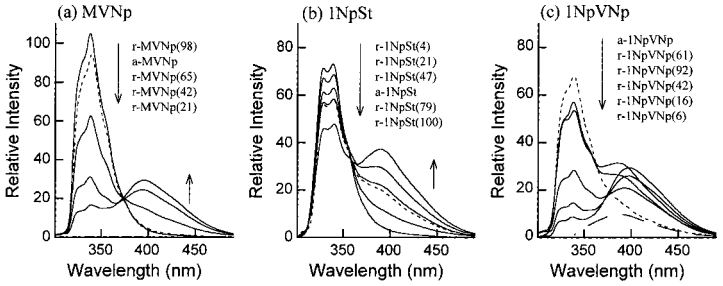


Fig. 2. Fluorescence spectra of alternating and random copolymers in THF at room temperature: (a) r-MVNp(x) and a-MVNp, (b) r-1NpSt(x) and a-1NpSt, (c) r-1NpVNp(x) and a-1NpVNp; (—) random copolymers, (- - -) alternating copolymers, (– – –) difference spectrum obtained by subtracting the spectrum of r-MVNp(98) (normalized at 345 nm) from that of a-1NpVNp; $[Np]_{residue} = 5\times10^{-5}$ M, excitation wavelength, 281 nm, the peak intensities are normalized to that (1 0 0) of IPNp.

function $(I(t) = \sum a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2))$ (Table 2). Since the physical significance of triple exponential fits to decay data for aromatic polymers has already been demonstrated by Phillips et al. [8–11], we should note here that the lifetimes obtained here are only parametric. However, from the observations that the above polymers have similar lifetimes and that the excimer emission, monitored at 440 nm, had a rise component with a time constant of ≈7 ns, it can be safely said that the same excimer is formed dynamically in these polymers.

The mode of intramolecular excimer formation in a polymer chain is conveniently estimated by investigating the ratio of excimer-to-monomer fluorescence intensity (I_E/I_M) as a function of the composition of copolymers [12,13]. Fig. 3 shows the plots of I_E/I_M against x in the copolymer. The upward curvature for r-MVNp(x) means that the excimer is formed preferentially in a contiguous sequence of aromatic residues: in fact, the I_E/I_M value is proportional to the diad fraction of the VNp residues up to ≈0.6 (data not shown), which is in agreement with the previous results [13,14]. In contrast, r-1NpSt(x) showed a linear relationship between I_E/I_M and x as in the case of poly(1NpMMA-co-MMA) [15]. This simple dependence of I_E/I_M on the chromophore density in a polymer chain leads to the conclusion that an excimer can be formed by either the nearest or non-nearest neighbours in this type of polymers. The same values of I_E/I_M for r-1NpSt(47) and a-1NpSt confirm this result.

Fig. 2(c) shows the fluorescence spectra of r-1NpVNp(x) and a-1NpVNp. The excimer emission for r-1NpVNp(x) was blue-shifted with increasing values of x: the excimer fluorescence emitted from the VNp units decreased and the one from the 1NpMMA units increased. On the other hand, a-1NpVNp showed strong monomer fluorescence but with some tailing in the long-wavelength region. This tail emission was assigned to the excimer formed in the alternating 1NpMMA sequences because of the following: (1) a-1NpSt showed excimer emission, but a-MVNp did not, as described above, (2) the difference spectrum obtained from subtracting the spectrum of r-MVNp(98) from that of a-1NpVNp exhibited a broad emission peaking at 390 nm which was identical with those for r-1NpSt(x) (Fig. 2(c)), (3) the emission for a-1NpVNp had almost the same time constants (lifetimes) as those for a-1NpSt (Table 2), (4) little excimer formation between 1-Np and 2-Np chromophores has been reported [4].

It should be noted that the monomer emissions for a-1NpVNp and all r-1NpVNp(x), except r-1NpVNp(92), were rather similar to those for a-MVNp and

Table 2
Fluorescence decay parameters for alternating Np polymers in THF[a]

Polymer	(τ_i/ns)/a_i			
	Monomer		Excimer	
r-MVNp(42)	20.1/0.23	7.5/0.77	46.0/1.32	10.8/−0.32
a-MVNp	51.3/1.00			
r-1NpSt(47)	45.1/0.61	11.9/0.39	50.7/6.96	6.6/−5.96
a-1NpSt	49.4/0.67	10.8/0.33	52.4/4.31	7.0/−3.31
r-1NpVNp(42)	21.4/0.32	7.7/0.68	52.0/1.58	8.4/−0.58
a-1NpVNp	45.6/0.75	12.7/0.25	52.4/2.58	8.0/−1.58

[a] Decay curves are analysed by using the equation: $I(t) = \sum a_i \exp(-t/\tau_i)$, excitation wavelength, 280 nm, emission wavelengths, 330 nm for the monomer and 440 nm for the excimer.

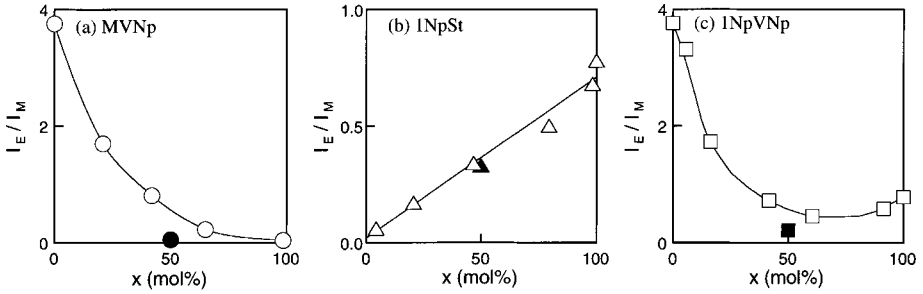


Fig. 3. Excimer-to-monomer fluorescence intensity ratio (I_E/I_M) as a function of x: (a) (○) r-MVNp(x) and (●) a-MVNp; (b) (△) r-1NpSt(x) and (▲) a-1NpSt, (c) (□) r-1NpVNp(x) and (■) a-1NpVNp. The I_M and I_E values are the intensities at the emission maximum for the monomer and excimer emissions, respectively.

r-MVNp(x), which is indicative of the fluorescence being emitted predominantly from the VNp units in all of these polymers. We may thus imagine that energy transfer from the 1NpMMA units to the neighbouring VNp ones occurs. Based on the fact that the absorption bands for a-MVNp are slightly red-shifted compared with those for a-1NpSt (Fig. 4), this transfer is energetically allowed. Here the question arises whether the energy transfer in the opposite direction, from the VNp units to the 1NpMMA ones, can occur or not. This point will be discussed on the basis of the effect of temperature on the fluorescence spectra in Section 3.2.

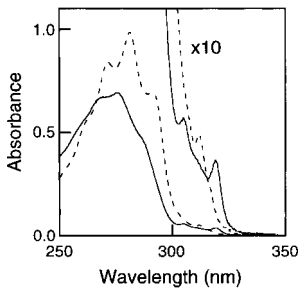


Fig. 4. Absorption spectra of (—) a-MVNp and (– – –) a-1NpSt in THF. $[Np]_{residue} = 1.5 \times 10^{-4}$ M.

3.2. Temperature dependence of fluorescence spectroscopy

Fig. 5 shows the fluorescence spectra of alternating copolymers in 1,4-dioxane observed at temperatures of 20–60°C. The monomer emission of a-MVNp slightly decreased with increasing temperatures, as well as that of r-MVNp(98), a model polymer showing no excimer emission (data not shown). This is clearly due to the increased radiationless deactivation processes for the Np chromophores themselves. For a-1NpSt, the excimer emission decreased moderately, while the monomer one decreased only slightly and the extent of the decrease was smaller than that for r-1NpSt(4) (data not shown). It is known that the intramolecular excimer formation process in polymer systems competes with the dissociation of the excimer or dimer to the monomers in these temperature regions [16]. Thus, the observation for a-1NpSt suggests that the dissociation process is facilitated at high temperatures. In contrast, the monomer emission of a-1NpVNp decreased largely in spite of a decrease in the excimer emission intensity. Then, the apparent participation of the excimer dissociation in the monomer emission should be minor. Considering the fact that the fluorescence quantum yield for the VNp unit is estimated to be higher than that for the 1NpMMA one (Fig. 2), it may be expected that the contribution of the monomer fluorescence emitted from

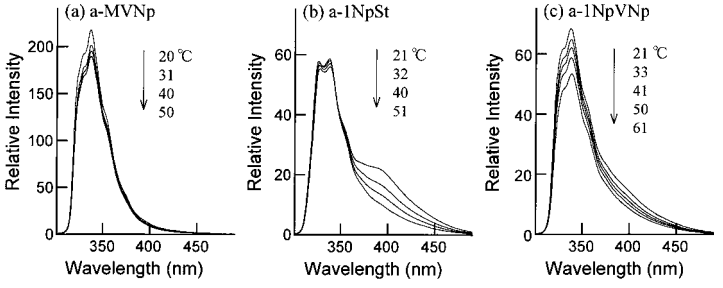


Fig. 5. Temperature dependence of fluorescence spectra of alternating copolymers in 1,4-dioxane: (a) a-MVNp, (b) a-1NpSt, (c) a-1NpVNp. $[Np]_{residue} = 5 \times 10^{-5}$ M, excitation wavelength, 281 nm, the peak intensities are normalized to that (1 0 0) of IPNp.

Table 3
Fluorescence quenching for alternating polymers by CCl_4 in THF[a]

Polymer	$\langle\tau\rangle$ (ns)	K_{SV} (M^{-1})	k_q ($M^{-1}\,s^{-1}$)
a-MVNp	51.3	101	2.0×10^9
a-1NpSt	45.6	62.7	1.4×10^9
a-1NpVNp	42.8	95.7	2.2×10^9

[a] For details see Ref. [2], $\langle\tau\rangle$, the weight–average fluorescence lifetime, K_{SV}, the Stern–Volmer constant, k_q, the quenching rate constant.

the 1NpMMA units increased with the temperature, i.e., the energy transfer from the VNp units to the 1NpMMA ones may occur to some extent at high temperatures. Therefore, we believe for 1NpVNp-type polymers that the one-way energy transfer from the 1NpMMA units to the VNp ones occurs favourably at room temperature and the two-way transfer becomes possible at higher temperatures. We further speculate that the corresponding 2-Np polymer, a-NpVNp, allows this two-way transfer more easily than a-1NpVNp, because the former polymer has practically the same chromophores [3]. As has been pointed out by Guillet [16], however, great care should be taken in interpreting the data on these steady-state emission intensities quantitatively. However, no further investigation has been done with this.

3.3. Fluorescence quenching

In the same manner as reported previously [2], the fluorescence quenching of alternating copolymers by carbon tetrachloride was examined. The quenching parameters obtained are listed in Table 3. There was only a little difference in the second-order quenching rate constants (k_q) among the polymers. This may be partially because the nearest-neighbouring Np groups in a-1NpVNp are not the same chromophores, diminishing the migration efficiency itself. Thus, the predominant one-way energy transfer may be unsatisfactory for the long-range energy migration along the polymer chain. Further, the intrinsic efficiency of Np chromophores might still be insufficient for the migration.

4. Conclusion

Excimer formation in the alternating methacrylate sequences is found to be uninhibited perfectly in a-1NpVNp, which is common to this type of Np polymers. The temperature dependence of the fluorescence spectra suggests that the two-way energy transfer becomes possible at high temperatures and may be more favourable for a-NpVNp than for a-1NpVNp. However, no remarkable facilitation of overall singlet-state energy migration along the polymer chain has been achieved for all copolymers. The predominant one-way energy transfer and/or the insufficient migration efficiency of Np chromophores themselves might be responsible for this. We note here that the efficient triplet-state energy migration occurring in a-NpVNp and a-1NpVNp is demonstrated by the observation of the delayed emission spectra. Details on this will be reported in the near future [17].

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