Studies of the Antenna Effect in Polymer Molecules. 6. Singlet Electronic Energy Transfer and Migration in Poly(2-vinylnaphthalene-*co*-9-anthrylmethyl methacrylate)

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ABSTRACT: Intramolecular transfer of singlet energy in 2-vinylnaphthalene polymers containing small amounts of the low-energy acceptor comonomer 9-anthrylmethyl methacrylate was studied by using both steady-state and transient fluorescence measurements. The migration coefficient of the excited naphthalene singlet was estimated to be of the order of 10^{-5} cm^2/s in 2-methyltetrahydrofuran glass at 77 K. In tetrahydrofuran fluid solutions, the transfer rate was greatly enhanced but the transfer from the naphthalene excimer to anthracene was found to be negligible compared with transfer from the excited naphthalene singlet.

Introduction

The kinetics of intramolecular excimer formation and of singlet electronic energy transfer in synthetic aromatic polymers have received considerable attention over the past two decades. In particular, synthetic polymers containing pendant naphthalene groups of a wide range of structures have been examined in great detail.[1–6] The understanding so achieved has led to some significant applications. Excellent examples are the studies of polymer compatibility utilizing excimer formation in naphthalene-containing polymers by Frank and co-workers.[7,8] Concurrently, in the field of solar energy conversion research, naphthalene-containing polymers have been studied as models for molecular antenna.[9–13]

Studies on the properties and efficiency of singlet electronic energy transfer to a small amount of polymer-bound energy traps (acceptors) in some naphthalene-containing polymers have been reported.[9] The high efficiencies exhibited by these polymers to harvest external light energy have been interpreted in terms of efficient singlet energy migration among identical naphthalene chromophores prior to trapping by the low-energy bound acceptors. This phenomenon has also been demonstrated in phenanthrene-containing polymers.[14–16] The latter system further allows quantification of the extent of migration due to its relatively simple photophysical properties.

In most cases of naphthalene-containing polymers, intramolecular excimers act as an additional channel for deactivation of the excited naphthalene singlet. Thorough understanding of this complex photophysical process and its competition with other energy acceptors for the monomeric excited naphthalene singlet (M*) is still lacking. The transfer of singlet energy from the excimer to a low-energy trap has been documented;[17] however, the relative importance of this process is yet to be established.

In designing a polymeric antenna, it is important to determine whether the concentration quenching of M* through intramolecular excimer formation constitutes an irreversible energy sink. However, if the excimer can transfer the excitation energy to the low-energy trap with appreciable efficiency or rapidly dissociate back to the excited monomer state through thermal activation, it might not affect the efficiency of energy migration. Excimer dissociation in aromatic polymers has been studied in many laboratories, but the results are still contradictory.[18–22,26,27]

Experimental Section

2-Vinylnaphthalene (2VN). 2-Vinylnaphthalene (10 g, Aldrich) was dissolved in 100 mL of cyclohexane and filtered. After removal of the solvent, the 2VN was chromatographed on alumina, eluting with cyclohexane, and appeared as the first band off the column. The crude product was fractionally sublimed twice at 40 °C. The above procedure gave rise to a 75% yield in purified monomer.

9-Anthrylmethyl Methacrylate (AMMA). To a solution of 5 g of dry 9-anthracenemethanol (Aldrich) in 65 mL of dry THF and 1 equiv of dry triethylamine was added 3 g of distilled methacryloyl chloride dropwise with stirring. After the reaction mixture was allowed to reflux for 1 h, the product was dissolved in ether and an aqueous workup with H_2O, 1 M HCl, 5% $NaHCO_3$, and saturated NaCl solution followed. The final ether extract was dried over $MgSO_4$. After removal of the solvent, the product was chromatographed on alumina, eluting with 2:1 benzene–cyclohexane. The product is the second band off the column and may be detected by TLC where $R_f = 0.35$ in 2:1 benzene–cyclohexane. The ester, purified by repeated recrystallization from cyclohexane, was obtained as yellow crystals. The methacryloyl chloride used in this synthesis was prepared from methacrylic acid and benzoyl chloride followed by fractional distillation.

Methyl Methacrylate (MMA). This monomer was obtained from Matheson Coleman and Bell and was washed with 1 M NaOH and dried over $MgSO_4$. The methacrylate ester was refluxed over calcium hydride and vacuum distilled under nitrogen.

Copolymers of 2VN and AMMA were prepared by AIBN-initiated radical polymerization in degassed benzene at 60 °C. They were allowed to polymerize for 9 h, resulting in products of approximately 15% yield (0.2 g). The copolymers were purified by two precipitations from benzene into methanol, washed with methanol and spectroscopic grade *n*-pentane, and dried under vacuum at room temperature.

The mole fraction of anthracene in the copolymers was determined by UV spectroscopy; the measured extinction coefficients of 9-anthrylmethyl pivalate (AMP) and 9-methylanthracene (MA) were used to approximate that of the polymer-bound anthracene. Similarly, the mole fraction of naphthalene in the copolymers was determined by comparison with the homopolymer of 2VN.

The molecular weights of the polymers were determined by means of a Mechrolab Model 502 automatic membrane osmometer.

Steady-state fluorescence spectra were recorded with a Hitachi MPF-2A spectrophotometer with phototube response corrected. For low-temperature measurements, the sample cell was a 3-mm-diameter quartz tube. Samples were purged with dry nitrogen and then slowly immersed in liquid nitrogen in a quartz Dewar (the phosphorescence accessories to the spectrometer).

The relative intensities of emissions from individual emissive components in these copolymers were obtained by using a procedure similar to that described by Holden and Guillet.[9] The fluorescence spectrum of AMP showed that the highest energy anthracene band rises steeply at 380 nm, so that the 350–375-nm emission in the copolymer is produced only by naphthalene monomer and excimer. It is therefore possible to reconstruct the

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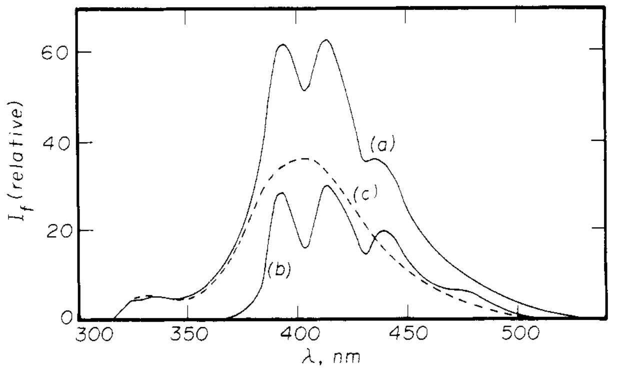


Figure 1. Steady-state fluorescence spectrum of poly(2VN-*co*-AMMA) (0.31% AMMA) in deoxygenated THF at 25 °C: (a) λ_{ex} = 280 nm, (b) λ_{ex} = 366 nm, (c) P2VN in THF at 25 °C, λ_{ex} = 280 nm.

Table I
Compositions and Molecular Weights of Poly(2VN-*co*-AMMA)

sample	monomer feed ratio, mol % 2VN:AMMA	polymer composition, mol % 2VN:AMMA	$\overline{M}_n$ $(10^5)^a$
1	100:0	100:0	1.20
2	99.8:0.2	99.69:0.31	1.26
3	99.6:0.4	99.50:0.50	1.10
4	99.4:0.6	99.26:0.74	1.31
5	99.3:0.7	99.05:0.95	0.93
6	99.2:0.8	98.91:1.09	1.38
7	99.0:1.0	98.75:1.25	1.01

[a] Membrane osmometry.

symmetric excimer band, which lies partially obscured by anthracene fluorescence, using the resolved spectrum of P2VN as a guide. The precision of this method is estimated to be ca. ±15%.

Fluorescence decays were recorded by a single-photon-counting apparatus of standard design.[23] The naphthalene chromophore was excited at 280 nm and its emission was monitored through the Jarrell-Ash monochromator, first at 337 nm and then through an additional band-pass filter (Corning 7-51, 310–410-nm bandpass) to minimize scattering light entering the photomultiplier.

The fluorescence decay curves were analyzed by using the iterative deconvolution technique.[24] The procedure for obtaining the asymptotic exponential decay rate is essentially taking the longest best-fit relaxation time (τ) in a multiexponential fit. Details of testing for reliability of the decay rate assignment have been described in an earlier publication.[15]

Results and Discussion

The steady-state fluorescence spectrum of poly(2VN-*co*-AMMA) (0.3% AMMA) in THF fluid solution is shown in Figure 1. The fluorescence spectrum of poly(2-vinylnaphthalene) (P2VN) is also shown for comparison. Substantial emission intensity characteristic of a 9-alkyl-substituted anthracene chromophore was observed superimposed on the naphthalene excimer emission band when the sample was excited at 280 nm. In view of the small fraction of incident photons at 280 nm being absorbed by the polymer-bound AMMA directly (less than 0.05%), intramolecular energy transfer from the initially excited naphthalene to anthracene is expected to be responsible for the high anthracene emission intensity.[9,15]

The copolymerization data and the molecular weights of the copolymer series studied here are listed in Table I. The emission intensity of each sample in fluid solution was resolved into its naphthalene monomer (M*), excimer (D*), and anthracene (A*) components. The fluorescence spectrum of the polymer-bound AMMA upon direct excitation (Figure 1b) (λ_{ex} = 366 nm) was taken as the standard for the anthracene component. The resolved spectrum of P2VN was used as a reference for the monomer and excimer emissions. The relative emission intensity of each component, I_X (X = A, M, or D), is determined from the area under the resolved fluorescence spectra. To study the dependence of the relative intensities of the various components on the AMMA content, the ratios I_A/I_M, I_D/I_M, and I_A/I_D are plotted against the mole fraction of polymer-bound AMMA (f_{AMMA}) and are shown in Figure 2a,b. It is seen that both I_A/I_M and I_A/I_D increase approximately linearly in f_{AMMA} for up to ca. 1.3 mol %. For convenience, we assume that the observed linearities can be extrapolated to f_{AMMA} = 1.5 mol %. On the other hand, I_D/I_M was found to be independent of f_{AMMA} over the same composition range. Furthermore, the ratios also conform to the empirical relation

$$I_A/I_M = (I_A/I_D)(I_D/I_M) \qquad (1)$$

to within experimental error. This finding further confirms the consistency of the spectral resolution procedure despite its crudeness.

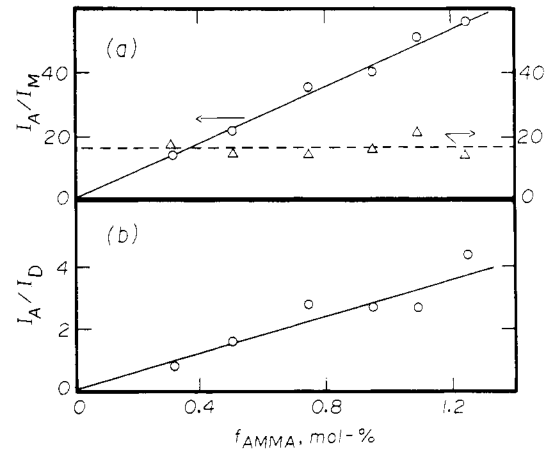
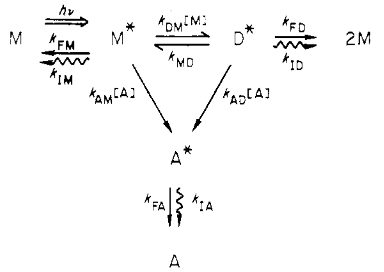


Figure 2. Variations of (a) I_A/I_M and I_D/I_M and (b) I_A/I_D with f_{AMMA} in poly(2VN-*co*-AMMA) in THF at 25 °C.

Scheme I



A kinetic scheme combining conventional excimer formation and decay with energy-transfer kinetics in the context of Stern–Volmer analysis can be represented by Scheme I.[17] In this scheme, k_{FX} and k_{IX} are the radiative and nonradiative decay rates, respectively, of the excited species X*, with X* = M* (monomer), D* (excimer), or A* (acceptor). The transfer rate constants from the monomers and excimers are denoted k_{AM} and k_{AD}, respectively, and the excimer formation and dissociation rates are given as k_{DM} and k_{MD}, respectively. Since the photophysical processes concerned here are strictly intrachain in nature, each concentration variable appearing in the kinetic scheme is understood to represent the local concentration of the species. These local concentrations are, in turn, related to the compositions of the copolymers. Under photostationary conditions, Scheme I predicts the following equations for the intensity ratios,

$$\frac{I_A}{I_M} = \frac{k_{FA}}{k_{FM}}\left\{\frac{k_{AM}}{k_{FM}} + \frac{k_{AD}k_{DM}[M]}{k_A(k_D + k_{MD} + k_{AD}[A])}\right\}[A] \quad (2)$$

$$\frac{I_A}{I_D} = \frac{k_{FA}}{k_{FD}}\left\{\frac{k_{AM}}{k_A}\left(\frac{k_D + k_{MD} + k_{AD}[A]}{k_{DM}[M]}\right) + \frac{k_{AD}}{k_A}\right\}[A] \quad (3)$$

$$\frac{I_D}{I_M} = \frac{k_{FD}}{k_{FM}}\left\{\frac{k_{DM}[M]}{k_D + k_{MD} + k_{AD}[A]}\right\} \quad (4)$$

where $k_X = k_{FX} + k_{IX}$, with X = M, D, or A. It should be noted that combination of eq 2–4 gives an expression for the relationship between the intensity ratios identical with the empirical formula given in eq 1. Further applications of eq 2–4 require relating the local acceptor concentration [A] to the acceptor mole fraction f_{AMMA} of the chains. In previous work[14,15] it was shown that in phenanthrene-containing polymers, f_{AMMA} of poly(phenanthrylmethyl methacrylate-*co*-anthrylmethyl methacrylate) was proportional to the local concentration of the AMMA chromophore for $f_{AMMA} \lesssim 1.5\%$. It is therefore a reasonable assumption that a linear relationship is also valid for this series of copolymers. Thus

$$[A] = \kappa_A f_{AMMA} \quad (5)$$

where κ_A is a proportionality constant relating to the chain dimensions in solution. Substituting eq 5 into eq 4 and rearranging give

$$\frac{(I_D/I_M)_0}{I_D/I_M} = 1 + \frac{k_{AD}}{k_D + k_{MD}}\kappa_A f_{AMMA} \quad (6)$$

with the subscript 0 denoting the ratio in the absence of any acceptor in the chain. Accordingly, the observed constancy of the ratio I_D/I_M over the range of f_{AMMA} values implies that

$$\frac{k_{AD}}{k_D + k_{MD}}\kappa_A f_{AMMA} \ll 1 \quad (7)$$

In order to compare the relative importance of the D* → A transfer and M* → A transfer, it is necessary to estimate the relative values of the two terms in eq 2. It is first noted that the observed linearity of I_A/I_M with f_{AMMA} (Figure 5) implies that the $k_{AD}[A]$ term in eq 2 can be neglected. Hence, the second term inside the braces in this equation can be rearranged and, combining with eq 7, satisfies

$$\left(\frac{k_{AD}\kappa_A f_{AMMA}}{k_D + k_{MD}}\right)\left(\frac{k_{DM}[M]}{k_A}\right) \ll \frac{k_{DM}[M]}{k_A} \quad (8)$$

Earlier studies of P2VN give estimates for $k_{DM}[M] \sim 1 \times 10^9\ s^{-1}$ [25] and $k_A^{-1} \sim 50 \times 10^{-9}$ s.[5] Furthermore, when 2-methylnaphthalene and MA are used as model compounds, k_{FA}/k_{FM} is estimated to be ca. 10.[17] One can now conclude that the second term in eq 2 satisfies

$$\left(\frac{k_{FA}}{k_{FM}}\right)\left(\frac{k_{DM}[M]}{k_A}\right)\left(\frac{k_{AD}\kappa_A f_{AMMA}}{k_D + k_{MD}}\right) \ll 50 \quad (9)$$

According to the experimental results shown in Figure 2, $I_A/I_M \sim 44 \times 1.5 = 66$ at $f_{AMMA} = 1.5\%$. By comparison with eq 9, it is concluded that the first term in eq 2 is dominant. Energy transfer from the excimer to the anthracene acceptor is therefore insignificant compared with transfer from the excited naphthalene monomers.

Dilute solutions of P2VN and poly(2VN-*co*-AMMA) in 2-methyltetrahydrofuran (2MTHF) glasses at 77 K do not show the usual structureless excimer emission but structured naphthalene monomer emission along with that of anthracene, indicating substantial energy transfer from naphthalene to anthracene (Figure 3). The fluorescence decay of the excited naphthalene in the P2VN homopolymer is single exponential. This permits an estimation of the extent of singlet energy migration among the naphthalene units in the polymers by using the transient fluorescence decay method.[15] The increment in the asymptotic decay rate, $k_m(\infty)$, of the donors (naphthalene) with the increase of the acceptor content measures the excitation mobility (the sum of mass diffusion and energy migration) in the chain. According to the model by Artamonova et al.,[28]

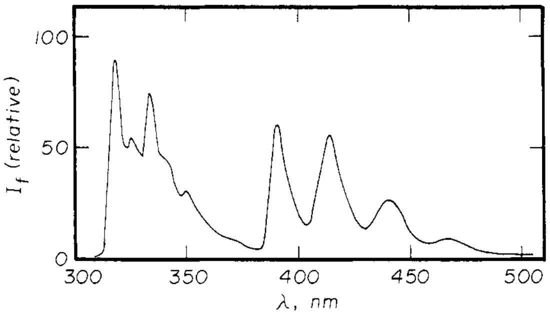


Figure 3. Steady-state fluorescence spectrum of poly(2VN-*co*-AMMA) (0.31% AMMA) in 2MTHF at 77 K. $\lambda_{ex} = 280$ nm.

$$k_m(\infty) = 4\pi\alpha_{DA}^{1/4}\Lambda^{3/4}[A] \quad (10)$$

where $\alpha_{DA} = (1/\tau_D^0)R_0^6$, with R_0 being the critical radius of Förster transfer, and Λ is the migration coefficient of the donor excitation. The latter constant has been determined for a series of phenanthrene-containing polymers to be ca. 1.5×10^{-5} cm^2/s.

In the present polymer system, the slope of the $k_m(\infty)$ vs. f_{AMMA} plot is comparable to that of the phenanthrene-containing polymers. In view of the similar order of magnitude for α_{DA} of the phenanthrene–anthracene pair (2.7×10^{15} Å^6 s^{-1}) and the naphthalene–anthracene pair (3.0×10^{15} Å^6 s^{-1}), one might expect that the migration coefficient Λ is also of the same order of magnitude in P2VN, that is, of the order of 10^{-5} cm^2 s^{-1}.

On the other hand, the increase of the excitation mobility due to segmental diffusion by raising the temperature to 25 °C cannot be determined by measuring $k_m(t)$ at this temperature since the fluorescence decay of the excited naphthalene monomer is now nonexponential. A crude estimate of this enhancement can be achieved by comparing the steady-state measurements of I_A/I_M at each temperature. At 77 K, the observed I_A/I_M measures a combined effect of direct naphthalene to anthracene transfer and transfer from an excited naphthalene to a distant anthracene trap through energy migration. This can be demonstrated by comparing the results of the steady-state and transient measurements. As mentioned earlier, the latter is capable of isolating the contribution to the excitation mobility due to energy migration. Recall that

$$I_A/I_M \sim (k_{FA}/k_{FM})(k_{AM}[A]/k_M) \quad (11)$$

The ratio k_{FA}/k_{FM} has been estimated previously to be ca. 10. The fluorescence lifetime k_M^{-1} was measured to be 77 ns. By identifying $k_{AM}[A]$ with $k_m(\infty)$, which has the effect of considering only the contribution of transfer from the migrating naphthalene singlets, $k_{AM}[A]$ is estimated to be $\sim 1.6 \times 10^6 \times f_{AMMA}$ from a plot of $k_M(\infty)$ vs. f_{AMMA} (Figure 4). Substitution of this value in eq 11 gives for $I_A/I_M(77\ K) \sim 1.3 \times f_{AMMA}$. Steady-state measurements of I_A/I_M vs. f_{AMMA} at 77 K give $I_A/I_M(77\ K) \sim 2.7 \times f_{AMMA}$, as shown in Figure 5. Comparison of the two results shows

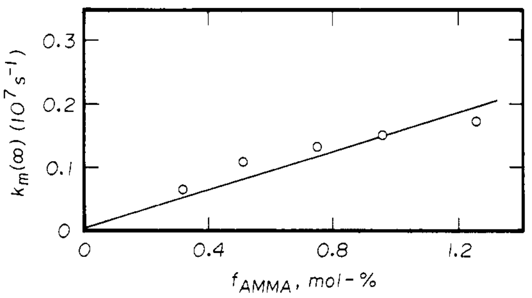


Figure 4. Variation of $k_m(\infty)$ with f_{AMMA} in poly(2VN-*co*-AMMA) in 2MTHF at 77 K.

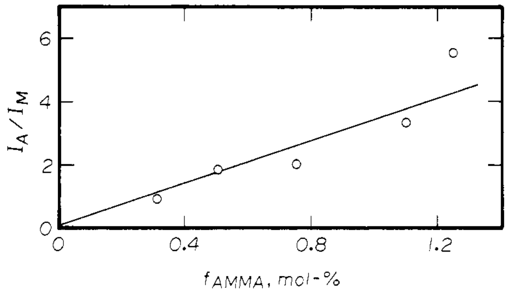


Figure 5. Variation of I_A/I_M with f_{AMMA} in poly(2VN-*co*-AMMA) in 2MTHF at 77 K.

that energy migration accounts for about half of the overall transfer of N* → A.

At room temperature, I_A/I_M has increased by a factor of ca. 16. This increase is probably due to both segmental diffusion assisted migration of the excited naphthalene singlet and segmental motion enhanced dynamical quenching (direct N* → A transfer).

Conclusions

When copolymerized with a small number of low-energy AMMA acceptors, 2VN polymers have been found to be efficient antennas for harvesting photon energy. Using transient fluorescence decay measurements, singlet energy migration among the excited naphthalene units was shown to be significant, even in the low-temperature glassy solution. In dilute fluid solutions at room temperature, the transfer efficiency was found to be much enhanced. It is proposed that this is caused by increased migration due to intrachain segmental diffusion, which also increases the efficiency of direct single-step transfer to the anthracene trap. The transfer from intrachain excimers to the anthracene traps was also demonstrated to be negligible compared with transfer from the excited naphthalene singlets.

The conventional Birks kinetic scheme, modified to include intrachain energy transfer, was found to be adequate to interpret the steady-state results presented here.

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Registry No. 9-Anthrylmethyl methacrylate-2-vinylnaphthalene copolymer, 84602-28-8.

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