Energy Transfer in Poly(2-vinylnaphthalene) Containing 9-Anthryl End Groups

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ABSTRACT: Energy transfer from 2-naphthyl to 9-anthryl chromophores in poly(2-vinylnaphthalene) containing 9-anthryl end groups (P2VN-A) was studied in dilute solution and in poly(methyl methacrylate) (PMMA) films by fluorescence techniques. Excimer formation in P2VN-A and its corresponding homopolymer was studied also. The efficiency of energy transfer from the naphthyl chromophores of the polymer chain to the 9-anthryl end group was determined and was found to vary from 10% to 88% under different conditions of solvent, substrate, and temperature. The highest transfer efficiency is obtained when P2VN-A is dispersed in solid PMMA films where a high-energy excimer emission is observed. It is proposed that these excimers promote energy transfer by providing a gradually decreasing energy transport pathway from the excited naphthyl chromophores to the 9-anthryl end groups.

Introduction

Photosynthesis uses absorbed light to drive a sequence of reactions which produces carbohydrates. The light-absorbing molecules (pigments) are grouped into a cluster of several hundred molecules which is called an antenna complex. Each antenna complex serves to collect light energy and transfer it to a single reaction center where the initial electron-transfer step in photosynthesis takes place. In this way, incident light is efficiently collected without the necessity of having a reaction center associated with every pigment molecule and the absorptivity of the reaction site is effectively increased several hundred fold.[1,2] An analogous situation exists in macromolecules which have suitable light-absorbing donor chromophores ("antennae") and energy acceptors ("reaction centers"). The excited-state processes occurring in such polymers have been studied widely.[3-16] Some of these polymers may have commercial applications which include sensitization of photooxidation–reduction reactions[14] and stabilization against photodegradation.[15,16] Light-harvesting polymers may also prove to be of importance in the catalysis of photochemical reactions where the acceptor may initiate a sequence of reaction steps.

In polymers containing aromatic substituents, excimer formation between an excited and ground-state chromophore can affect the energy-transfer that occurs to specific energy acceptor sites incorporated in the polymer chain. The mechanism of excimer formation and its role in the energy-migration process have been discussed widely in the literature for synthetic polymers such as poly(styrene),[17] the poly(vinylnaphthalenes),[17,18] poly(acenaphthalene),[18] and poly(1-naphthyl methacrylate).[19] It is generally believed that excimer sites act as traps for the migrating energy and may thus reduce energy transfer to acceptor groups. Studies carried out on bichromophoric model compounds[20-22] lead to the general conception of an intramolecular excimer being a "sandwich-type" dimer structure in which the aromatic components (separated by a distance corresponding to three carbon atoms) are aligned in a periplanar configuration at a distance of approximately 300 pm. However, not all excimers rigidly adopt this configuration. In the case of poly(vinylcarbazole), for example, one of the two excimer emission bands is attributed to a partially eclipsed configuration of the carbazole chromophores.[23,24]

The role of excimer formation in the singlet energy sensitization of pyrene by naphthalene in poly(2-vinylnaphthalene) (P2VN) is described by Hargreaves and Webber.[25] Similar work by Guillet and co-workers[5-10] on polymer systems containing naphthalene and anthracene chromophores is documented extensively. The present study aims to characterize P2VN containing 9-anthryl end groups (P2VN-A) by steady-state and time-resolved fluorescence techniques.

Experimental Section

Materials and Preparations. 2-Vinylnaphthalene (2VN) (Polysciences) was purified by vacuum sublimation and methyl methacrylate (MMA) (Koch-Light) was distilled before use. The 9-(chloromethyl)anthracene (Alfa Division) reagent was used as received. Benzene, toluene, diethyl ether, and ethanol were purified by distillation. Methanol (Merck, spectroscopic grade) and tetrahydrofuran (THF) (Unichrom, HPLC grade) were used as supplied. Each solvent was observed to be free of all fluorescent impurities in the spectral region of interest.

Poly(2-vinylnaphthalene) (P2VN) was synthesized from its monomer by using azobis(isobutyronitrile) (AIBN) initiated radical polymerization in benzene. The 9-anthryl end groups were incorporated in the P2VN chains by polymerizing the monomer in the presence of 9-(chloromethyl)anthracene, which behaves as a chain-transfer agent. Five freeze–pump–thaw cycles were used to degas the monomer solutions before polymerization. The solutions were maintained under vacuum in an air oven at 70 °C for 60–72 h during polymerization. The polymers were purified by multiple reprecipitations from benzene into methanol. The weight-average molecular weight of the polymer, determined by low-angle light scattering measurements, was 9500. Gel permeation chromatography indicated a polydispersity (M_w/M_n) of 1.5. The average number of anthracene moieties per polymer chain was estimated to be 0.33 when the absorption spectrum of a solution of P2VN-A was compared to that of a solution of 9-methylanthracene of known concentration. The absorption spectra were recorded on a Hitachi Model 150-20 spectrophotometer.

Polymeric films were prepared by dissolving the polymers in toluene which contained 4% by weight of poly(methyl methacrylate) (PMMA). These solutions were then cast onto quartz slides. The films were air dried at room temperature and had an average thickness of 20 μm. Solutions of the polymers in pure solvents were degassed to less than 10 mTorr before analysis. The optical density of each polymer solution was measured at room temperature and was found to be approximately 0.2 at the excitation wavelength.

Steady-State Fluorescence Spectra. Uncorrected fluorescence emission spectra of samples in degassed, purified solvents were recorded on a Perkin-Elmer MPF-44A spectrofluorimeter. Temperatures were maintained at 25 °C by using water circulation which was controlled by a Braun Thermomix 1420 temperature controller. At low temperatures, emission spectra of polymer solutions which were placed in a cylindrical quartz tube (external diameter 1.1 cm) were obtained by using an Oxford Instruments DN704 liquid nitrogen cryostat. This device uses a DTC-2 variable-temperature controller (±0.1 K accuracy) and is adapted

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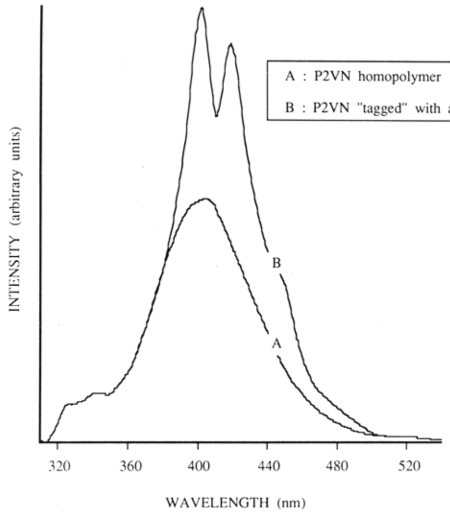

Figure 1. Steady-state fluorescence spectra of P2VN and P2VN-A in benzene at 25 °C.

with Suprasil B nonbirefringent windows.

Time-Resolved Fluorescence Spectra. Fluorescence decay profiles and time-resolved fluorescence spectra were recorded by single photon counting techniques using a mode-locked, cavity-dumped, synchronously pumped dye laser (Spectra Physics 171/375) as the excitation source. In this study, the 590 nm output from the dye laser was frequency doubled by using a temperature-tuned ADA crystal to generate vertically polarized light pulses at 295 nm (4 MHz). These were used to excite the naphthalene chromophores in the polymer samples. The fluorescence of the sample was detected through a polarizer set at 54.7° with respect to the plane of polarization of the excitation light to correct for any polarization effects on the fluorescence.[26] The emitted light was focused onto a Jobin-Yvon H-20 monochromator and detected by a Philips XP 2020Q photomultiplier tube. The total instrument response function for the single-photon-counting system was measured and was found to be approximately 400 ps at the full pulse width at half-height.

Fluorescence decay data were transferred to a VAX 11/780 computer and analyzed by using a nonlinear least-squares iterative reconvolution fitting procedure to the sum of one, two, or three exponentials. Goodness of fit was assessed by inspection of residuals, autocorrelation function, reduced χ-square value, and the Durbin–Watson parameter.[27,28] Time-resolved emission spectra were recorded by using the upper and lower level voltage discriminators on the output of the time-to-pulse height converter to select a "time window" in the decay profile. The monochromator was then synchronously scanned by using a multichannel analyzer operating in the "multichannel scaling" mode. These spectra were uncorrected for the wavelength response of the detection system.

Results and Discussion

The steady-state fluorescence spectrum of a dilute solution of P2VN homopolymer in benzene (Figure 1A) exhibits emission from the monomeric 2-naphthyl chromophores (320–350 nm), as well as a broad, structureless excimer emission (350–460 nm). The structured anthracene emission which is characterized by three emission maxima at 400, 420, and 445 nm (Figure 1B) is observed for a dilute solution of P2VN-A ($\approx 10^{-6}$ M) in addition to the monomeric and excimer fluorescence. The excitation wavelength used for both polymer solutions was 295 nm. At this wavelength, the naphthyl chromophores are responsible for greater than 99.9% of the fraction of light absorbed by each solution.

The detection of considerable amounts of anthracene and excimer fluorescence indicates energy transfer and energy migration from the pendant 2-naphthyl groups to the 9-anthryl end groups and to the excimer sites, respectively. The intense excimer emission (relative to the monomer emission) present in the steady-state fluorescence spectrum of the P2VN homopolymer suggests that efficient energy migration occurs to suitable excimer sites since the concentration of these sites is believed to be quite small (the fraction of chromophores in excimer-forming sites in P2VN is estimated to be 0.072[29]). It should be noted that dilute polymer solutions (10^{-5} to 10^{-6} M) were used in order to eliminate collisions between polymer chains during the excited-state lifetime.[17-20] Energy relaxation in these systems, therefore, originates from intrachain processes.

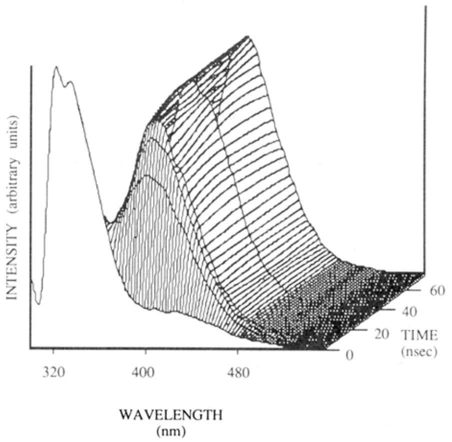

Figure 2. Area-normalized and time-resolved fluorescence spectra of P2VN in benzene at 25 °C (shading obtained by interpolation between individual spectra).

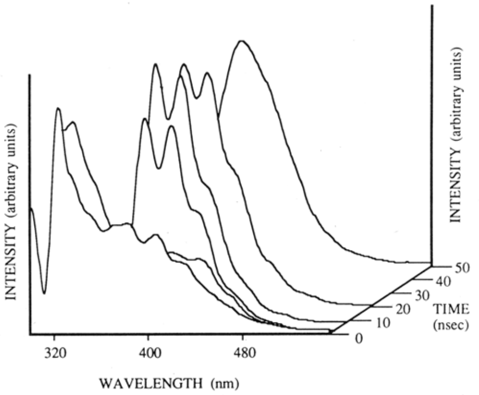

Figure 3. Area-normalized and time-resolved fluorescence spectra of P2VN-A in benzene at 25 °C.

The area-normalized time-resolved fluorescence spectra of P2VN (Figure 2) indicate that excimer emission is observed almost immediately after excitation. The excitation energy is localized on the excimers for a long period of time (>70 ns after excitation) and reverse dissociation of the excimer to reform the excited-state monomer does not occur. At late times (>50 ns) after excitation, no monomer emission was detected although there was some excimer fluorescence. This behavior is consistent with previous studies of P2VN[30] but differs from that reported for other polymers such as poly(1-vinylnaphthalene)[31-33] and poly(styrene)[34,35] where a spectral monomer component is observed at all times when excimer emission is present. This indicates that, in the last two polymers, an equilibrium is established between monomers and excimers during the excited-state lifetime. However, the excimers formed in P2VN appear to be relatively stable and can act as efficient traps for the migrating energy. In P2VN-A, very rapid (within 1 ns) energy transfer to anthryl moieties is observed (Figure 3).

Table I
Results of Fluorescence Decay Analyses

emission wavelength, nm	time constants, ns (±10%)			preexponential values, counts (±10%)			reduced χ^2
	τ_1	τ_2	τ_3	A_1	A_2	A_3	
315	0.8	2.9	16	20 000	10 000	350	1.9
325	0.7	2.6	21	21 000	10 000	250	1.9
390	0.9	9.9	46	-500	16 000	6600	1.7
470	2.6	8.5	34	-7 500	20 000	8200	1.9

Fluorescence decay profiles of P2VN-A were recorded at several emission wavelengths. A wavelength of 295 nm was used for excitation of the monomeric naphthyl chromophores. The decay profiles are poorly described by both single- and double-exponential functions but fit more reasonably to a triple-exponential function. The results that were obtained by using a sum of three exponentials are presented in Table I. The complex decay behavior may be attributed in part to the presence of chains without anthryl end groups. However, recent publications[36,37] have questioned the validity of associating time constants (derived from decay analyses) with the existence of distinct excited-state species and the subsequent generation of kinetic schemes. In particular it has been suggested that multistep electronic energy migration and transfer to trap sites inevitably leads to complex decay kinetics.[36,37] However, some general comments concerning the data in Table I can be made. The very short lifetime component ($\approx$0.8 ns) in the monomer decay (315 and 325 nm) corresponds to the rise time observed at a wavelength where anthracene emission is dominant (390 nm). This reflects the rapid rate of energy transfer to the anthryl end groups in the "tagged" polymer chains. The τ_2 component ($\approx$2.6 ns) in the monomer emission is observed as a rise-time component in the excimer region (470 nm), suggesting that this corresponds to the excimer formation process in the "untagged" chains. The excimer sites are characterized by a lifetime of about 40 ns and the anthracene fluorescence decays with a lifetime of about 9 ns. A very small contribution by a longer-lived component ($\tau \approx 20$ ns) in the monomer emission might be attributed to monomeric chromophores that are not participating in the energy-transfer or excimer-formation processes.

The energy-transfer efficiency (X%) for P2VN-A is defined as the ratio between the number of quanta transferred to anthracene and the number of quanta absorbed by naphthalene. The value of X may be calculated by using the equation $X/(1 - X) = \phi_N I_A/\phi_A I_N$ (eq 1), in which ϕ_N and ϕ_A are the fluorescence quantum yields obtained on direct excitation of the naphthyl chromophores and the anthryl end groups, respectively. The quantum yields of the degassed polymer solutions ($\phi_N = 0.18$ and $\phi_A = 0.58$) were determined relative to quinine bisulfate in 1 N H_2SO_4 ($\phi_F = 0.546$) by utilizing corrected emission spectra.[38] Fluorescence quantum yields of polymeric films ($\phi_N = 0.20$ and $\phi_A = 0.32$) were determined in a similar manner relative to sodium 4-(3′-phenyl-2′-pyrazolin-1′-yl)benzenesulfonate in a poly(vinyl acetate) film ($\phi_F = 0.92$).[39] I_N and I_A are the intensities of the non-anthracene and anthracene fluorescence, respectively.[40] The values of I_N and I_A were obtained after normalizing the fluorescence spectra of both P2VN and P2VN-A at 340 nm, the wavelength of monomer emission (see Figure 1). In the case of P2VN-A in solid films, I_N and I_A were obtained after normalizing the fluorescence spectra of P2VN-A and 9-methylanthracene at 480 nm. At this wavelength there is negligible excimer emission from the polymer (Figure 4). The energy-transfer efficiency values calculated by eq 1 are for polymer chains which contain one anthryl end group. The average number of anthryl moieties per polymer chain is estimated to be 0.33. Thus it is expected that the calculated "X values" underestimate the transfer efficiency by a factor of about 3.3.

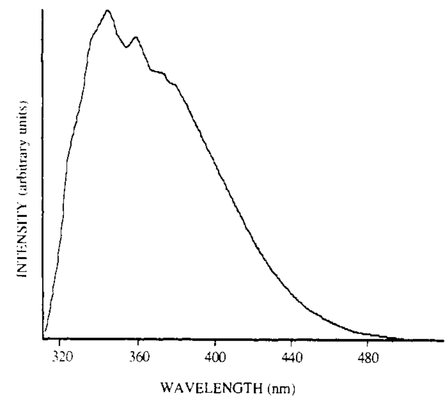

Figure 4. Steady-state fluorescence spectrum of P2VN in PMMA film.

The overall efficiency of energy transfer from naphthalene to anthracene chromophores in dilute solutions of P2VN-A in benzene at room temperature was found to remain effectively constant ($X = 10 \pm 1$%, from eq 1) upon addition of up to 80% of diethyl ether, a poor solvent. This suggests that most of the 2-naphthyl and 9-anthryl chromophores lie within a sphere characterized by the Forster radius of 2.1 nm,[41] which is the requirement for energy transfer to occur with 50% efficiency. At closer distances the energy-transfer process is expected to have an efficiency value which is greater than 50%. In the case of P2VN-A, the radius of gyration of the polymer coils is estimated to be 2.5 nm and a transfer efficiency value of 33% is calculated on the assumption that each polymer chain contains one anthryl moiety. This result suggests that other processes such as excimer formation compete effectively with the one-step Forster transfer to anthracene. The time-resolved spectra of P2VN indicate that excimer sites are highly stable and may act as efficient traps for the energy from the excited-state naphthyl chromophores.

Excimer formation in P2VN and P2VN-A is an energetically activated process and the analysis of fluorescence data over the temperature range 160–300 K using a simple Arrhenius relation gives an activation energy of about 10 kJ mol^{-1}. This value is slightly less than that required for rotation about a single carbon–carbon bond (12.6 kJ mol^{-1} for ethane[42]) and may be associated with the relatively small conformational changes that are required for excimer formation. The mobility of the polymer chains is restricted at low temperatures and excimer formation is suppressed consequently. A maximum value of $X = 22$% (an efficiency of 73% if there were one anthryl molecule per polymer chain) is obtained at 260 K. Significant blue-shifted excimer emission is observed at this temperature and the enhanced transfer efficiency may be due to the ability of these sites to assist in the transfer of energy to the anthryl moieties. A similar effect is observed when P2VN-A is incorporated in a film of poly(methyl methacrylate) (PMMA).

Figure 4 shows the steady-state fluorescence spectrum of P2VN incorporated in a film of PMMA in which the concentration of naphthalene chromophores is 1.3 M. At such a high concentration, energy migration between naphthalene chromophores on different polymer chains can occur. Partial phase separation of P2VN in blends with PMMA has been reported.[43] However, this phenomenon was not visually apparent in the samples investigated

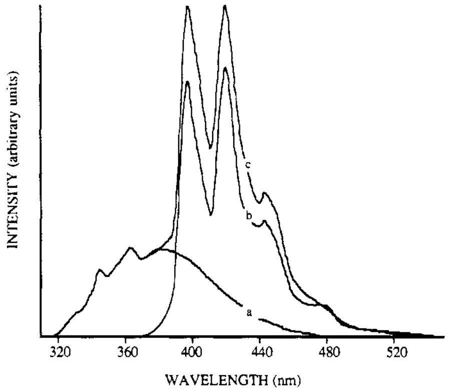

Figure 5. Steady-state fluorescence spectra of P2VN-A in PMMA film: (a) reconstruction of excimer band, (b) reconstruction of anthracene emission, and (c) fluorescence spectrum of P2VN-A in PMMA film.

here. The mobility of the P2VN chains in the PMMA film is impaired, but significant excimer emission is observed. The emission is blue-shifted (spectral maximum at 380 nm) compared with that observed in solution (maximum at 400 nm). The high-energy excimer emission may be attributed to partially eclipsed configurations of naphthyl chromophores which are "frozen-in" during film formation. A transfer efficiency value of 88% is obtained in the case of P2VN-A in PMMA at room temperature (see Figure 5). This suggests that the higher energy excimer sites can facilitate the energy-transfer processes in contrast to the low-energy excimer sites which act as efficient traps for the migrating energy. This may be due to a significant overlap between the emission of the high-energy excimers (band maximum at 380 nm) and the anthracene absorption (maxima at about 370 and 390 nm) which constitutes a necessary requirement for a Forster energy-transfer process.[44] Similar effects have been observed in alternating 2-vinylnaphthalene/methacrylic acid copolymers containing 9-anthryl end groups in which blue-shifted excimer emission and transfer efficiencies of greater than 90% were obtained.[45,46]

Conclusion

Excimer sites have been suggested to act as efficient traps for the migrating energy in aromatic polymers. In the case of P2VN, the excimers that are present when this polymer is incorporated in PMMA films are of higher energy than those observed in a dilute solution. Despite the presence of excimer emission, the energy-transfer efficiency from naphthalene to anthracene in PMMA films is calculated to be 88%. The formation of higher energy excimers appears to enhance the light-harvesting properties of P2VN-A by providing a transport pathway of decreasing energy from the naphthyl chromophores to the 9-anthryl end groups. The results suggest that the excimer configurations that are present in the polymer are crucial in determining the efficiency of the energy-transfer process from the excited naphthyl to the anthryl chromophores.

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Registry No. P2VN, 28406-56-6; PMMA, 9011-14-7.

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