Studies of the Antenna Effect in Polymer Molecules. 2. Singlet Electronic Energy Transfer in Phenanthrene-Containing Polymers by Transient Fluorescence Methods

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Received December 16, 1981

ABSTRACT: Singlet electronic energy transfer in poly[(9-phenanthryl)methyl methacrylate] (poly(PhMMA)), its copolymers with (9-anthryl)methyl methacrylate (AMMA), and its terpolymers with AMMA and methyl methacrylate (MMA) was studied by using transient fluorescence decay measurements, both in fluid solutions and in low-temperature rigid glass. Singlet energy migration among the donor molecules (phenanthrene) was found to be significant and increases with the donor content in the polymers. In 35/65 (v/v) MTHF/THF glass at 77 K, the migration coefficient of the singlet excitation in poly(PhMMA) homopolymer was estimated to be ca. 1.5×10^{-5} cm^2/s.

Introduction

The problem of singlet electronic energy migration in synthetic polymers has attracted much interest, both theoretically[1,2] and experimentally.[3-14] Despite considerable advances achieved over the past decade, the unambiguous identification of the process and its quantification remain a challenge. Critical reviews of the existing experimental evidence for the occurrence of singlet energy migration in polymers have been published recently.[15,16]

Due to the lack of direct experimental detection of the migration process, studies on such phenomena frequently require theoretical modeling and subsequent experimental verification. The basic mechanisms of nonradiative electronic energy transfer between a pair of chromophores are usually described by using the long-range dipole–dipole mechanism of Förster[17] or the short-range electron exchange interaction mechanism due to Dexter.[18] Statistical models are then devised to predict the overall transfer properties of a collection of chromophores in a system.

In the case where dipole–dipole interaction is expected to be the dominant mechanism of nonradiative transfer, Stern–Volmer kinetics and Förster kinetics describe the two extremes of the effect of chromophore mobility on the rate of energy transfer. The former is realizable when complete statistical "mixing" of the excited donor (D*) and the acceptor (A) occurs owing to material diffusion and/or excitation migration. This results in an enhanced rate of exponential decay of the transient donor fluorescence. Förster kinetics describes systems in which both D* and A remain effectively stationary during the transfer. The energy transfer rate decreases with time and, as a result, the donor fluorescence decay is nonexponential. The intermediate kinetics then represent the partial mixing of D* and A.

The technique of monitoring the donor fluorescence intensity with time upon pulsed excitation as a probe of energy transfer has been employed rather extensively in uniform systems in the condensed phase.[19-21] Solvents of a wide range of viscosities were used to control the mobility of the chromophores and good agreement with the theory was obtained under a wide range of conditions. The same technique has also been applied to the study of excitation mobility by energy migration among identical molecules.[22] Its application to aromatic polymers containing bound traps is more difficult due to many complicating factors associated with polymers. In particular, intramolecular excimer formation quenches the excited donor D* in a complex way. The inhomogeneous spatial distribution of the polymer-bound chromophores may also create complications in the analysis as the existing theories were primarily derived assuming a uniform distribution of chromophores. Furthermore, radiationless self-quenching of the excited donors can be important in some polymers because of the high local concentration of the chromophores.

Alternative techniques for studying migration in polymers include fluorescence depolarization,[23-25] small-molecule quenching,[3,7,26,27] and kinetic studies of intramolecular excimers.[9,12] These either fail to yield conclusive evidence for energy migration or do not provide quantitative estimates of the extent of energy migration in aromatic polymers.

This paper describes singlet energy migration in the new phenanthrene-containing polymers whose synthesis and properties were reported previously. The donor fluorescence decay is used to measure the extent of energy migration in the chain. The suitability of this approach is based on the findings that the phenanthrene-containing polymers do not form excimers or undergo self-quenching, and in the absence of any acceptor, the fluorescence decay is single exponential.[28]

Theory

The transient intensity of the donor fluorescence after a δ-pulse excitation can be written in the form

$$I_{D^*}(t) = I_{D^*}(0) \exp\{-[(1/\tau_D^0) + k_m(t)]t\} \quad (1)$$

where $1/\tau_D^0$ is the fluorescence decay rate of an ensemble of donors in the absence of acceptors. The time-dependent rate constant $k_m(t)$ describes the increase in the decay rate as a result of energy transfer to the low-energy traps.

Förster Kinetics. When dipole–dipole interaction is the dominant transfer mechanism, in a system of noninteracting donors surrounded by randomly distributed acceptors with both D* and A remaining stationary during the lifetime of D*, $k_m(t)$ is given by[29]

$$k_m(t) = 2(C_A/C_A^0)(t\tau_D^0)^{-1/2} \quad (2)$$

In eq 2, C_A is the bulk acceptor concentration (molecule/cm^3) and C_A^0 is the critical acceptor concentration given by

$$C_A^0 = [(4\pi/3)R_0^3]^{-1} \quad (3)$$

where R_0 is the Förster critical radius[30] of transfer defined as

$$R_0^6 = \frac{9000 \ln 10 \kappa^2 \Phi_{D^*}^0}{128\pi^5 N n^4} \int_0^\infty \frac{I_D(\bar{\nu})\epsilon_A(\bar{\nu})\, d\bar{\nu}}{\bar{\nu}^4} \quad (4)$$

In eq 4, ϵ_A is the extinction coefficient of A, I_{D^*} is the

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relative fluorescence intensity of D* at $\bar{\nu}$ satisfying $\int_0^\infty I_{D^*}(\bar{\nu})\, d\bar{\nu} = 1$, $\Phi_{D^*}{}^0$ is the fluorescence quantum yield of D* in the absence of the acceptor, n is the refractive index, and κ^2 is a molecular orientation factor. If the transition dipoles are averaged over a random distribution of orientation, κ^2 takes the value of $^2/_3$. Thus, according to the Förster scheme, the donor fluorescence at short times should demonstrate the characteristic $t^{1/2}$ dependence and at long times, $k_m(t)$ approaches zero asymptotically. If the exchange mechanism is dominant, $k_m(t)$ also vanishes at long times but obeys a rather different time-dependent function at short times.

Intermediate Kinetics. This is the regime where the mean diffusion distance $\langle r^2 \rangle^{1/2}$ during the D* lifetime is comparable to R_0, the Förster critical transfer radius. Several theoretical models have been developed.[31] Only that of Yokota and Tanimoto,[32] which is developed from Förster mechanism, and that of Voltz et al.,[33] which is developed from diffusion theory, will be reviewed here.

Yokota and Tanimoto introduced the Förster transfer rate as a pair-interaction function to the diffusion equation for the distribution function of [D*]. The equation was then solved by using the Padé approximant to obtain an analytical expansion for $I_{D^*}(t)$ given as

$$I_{D^*}(t) = I_{D^*}(0) \exp[(-t/\tau_D{}^0) - 2B(C_A/C_A{}^0)(t/\tau_D{}^0)^{1/2}] \quad (5)$$

where

$$B = \left(\frac{1 + 10.87x + 15.5x^2}{1 + 8.743x} \right)^{3/4}$$

with

$$x = D\alpha_{DA}{}^{-1/3} t^{2/3} \quad (6)$$

and

$$\alpha_{DA} = R_0{}^6/\tau_D{}^0 \quad (7)$$

Notice that eq 5 reduces to Förster kinetics when $B = 1$, which is the case when molecular diffusion is negligible ($D \simeq 0$).

The model developed by Voltz et al. is based on Noyes's diffusion theory.[33] By making two assumptions—identifying the reaction probability per collision in this theory with the transfer probability and setting its value to 0.5, and replacing the sum of collision radii R by the critical transfer radius R_0—they obtained the following expression for $k_m(t)$:

$$k_m(t) = 4\pi R_0 D C_A [1 + R_0(\pi D t)^{-1/2}] \quad (M^{-1}\ s^{-1}) \quad (8)$$

Therefore, the D* fluorescence decay is given by

$$I_{D^*}(t) = I_{D^*}(0) \exp[(-t/\tau_D) - 2At^{1/2}] \quad (9)$$

where

$$1/\tau_D = 1/\tau_D{}^0 + k_m(\infty) \quad (10)$$

with

$$k_m(\infty) = 4\pi R_0 D C_A \quad (11)$$

and

$$A = 4R_0{}^2(\pi D)^{1/2} C_A \quad (12)$$

In many earlier applications of these theories to studying energy migration, the diffusion constant D was generalized to account for the overall mobility of the donor excitation due to the combined effect of diffusion and migration ($D + \Lambda$).

In the case that the excitation mobility is primarily due to migration, a random walk model developed by Artamonova et al.[34] provides a good basis for the understanding of the kinetics.[35] In this model, the donor fluorescence decay is given by the following expression:

$$I_{D^*}(t) = I_{D^*}(0) \left\langle \prod_{\substack{j\text{th} \\ \text{acceptor}}} \exp\left\{ -\int_0^t k_{DA_j}[R_{DA_j}(t')]\, dt' \right\} \right\rangle \exp(-t/\tau_D{}^0) \quad (13)$$

where $k_{DA_j}[R_{DA_j}(t)]$ is the probability of quenching by the jth acceptor at time t and the angular brackets here mean average over the ensemble of all the possible realizations of the excitation trajectory. This model predicts that at long times, the donor fluorescence decay approaches exponential, with $k_m(\infty)$ given by

$$k_m(\infty) = 4\pi\alpha_{DA}{}^{1/4} \Lambda^{3/4} C_A \quad (14)$$

where α_{DA} and C_A were defined earlier and Λ, the migration coefficient, is given by

$$\Lambda = (1/2)(4\pi/3)^{4/3} C_D{}^{4/3} \alpha_{DD} \quad (15)$$

where α_{DD} has a meaning similar to α_{DA}.

Stern–Volmer Kinetics. In the case where $D \gg R_0{}^2/t$ in eq 8, the transfer rate $k_m(t)$ becomes time independent. The donor fluorescence decay will be strictly single exponential with decay rate given by $1/\tau_D{}^0 + k_m$. In general, this condition can be satisfied when the excitation mobility (diffusion or migration) is high.

Experimental Section

Methyl methacrylate (MMA) (Matheson Coleman and Bell) was washed with 1 N NaOH and then dried over $MgSO_4$. The methacrylate ester was then refluxed over calcium hydride followed by vacuum distillation under nitrogen.

(9-Phenanthryl)methyl methacrylate (PhMMA) and (9-anthryl)methyl methacrylate (AMMA) were prepared by the Schotten–Bauman reaction of methacryloyl chloride with 9-phenanthrenemethanol and 9-anthracenemethanol, respectively.

Copolymers (poly(PhMMA–MMA)) and terpolymers (poly(PhMMA–MMA–AMMA)) were synthesized by AIBN-initiated free-radical polymerization in degassed benzene (Fisher, spectral grade) at 60 °C for ca. 4 h. The polymers were then purified by multiple reprecipitations from benzene into methanol and washed thoroughly with methanol and with spectral grade n-pentane. The samples were then further dried in vacuo over P_2O_5. Compositions were determined by UV absorption analysis and molecular weights by osmometry in dioxane solution.

Tetrahydrofuran (Caledon, spectral grade) and 2-methyltetrahydrofuran (2MTHF) (MCB) were refluxed over $LiAlH_4$ several times and then fractionally distilled.

Steady-state fluorescence spectra were recorded on a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter. 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, a phosphorescence accessory to the spectrometer. The solvent used was a 35/65 (v/v) mixture of 2MTHF/THF, which forms a clear glass at 77 K.

Fluorescence decays were recorded by single-photon-counting techniques.[38] The phenanthrene chromophore was excited at 280 nm and its emission was viewed through the Jarrell-Ash monochromator, first at 365 nm and then through an additional narrow-band interference filter (Balzer UV 365) to minimize scattering light entering the stop photomultiplier.

The fluorescence decay curves were analyzed by the iterative deconvolution technique.[39] The procedure for obtaining the asymptotic exponential decay rate will be discussed in detail in the Appendix.

Results and Discussion

The fluorescence decay of the homopolymer in deoxygenated THF at room temperature was found to be single exponential with a lifetime $\tau_D{}^0 = 44.3 \pm 0.5$ ns. This is

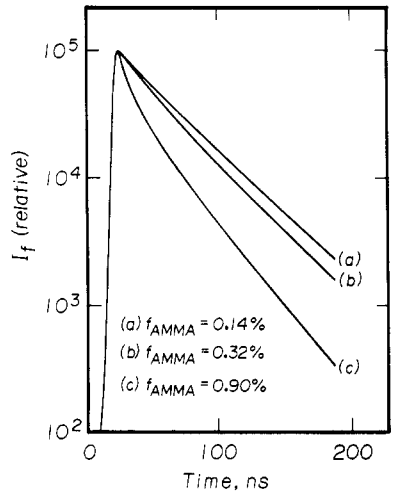

Figure 1. Transient donor fluorescence decay of poly(PhMMA–AMMA) in THF at 25 °C: time scale = 1.59 ns/channel, λ_{ex} = 280 nm, λ_{em} = 366 nm.

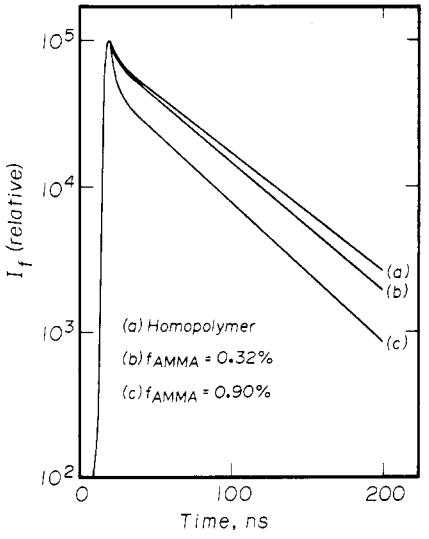

Figure 2. Transient fluorescence decay of poly(PhMMA–AMMA) in 2MTHF/THF glass at 77 K: time scale = 1.59 ns/channel, λ_{ex} = 280 nm, λ_{em} = 366 nm.

to be compared with that of the model compound (9-phenanthryl)methyl pivalate (PhMP) under the same conditions (τ_D = 45.5 ± 0.5 ns). In low-temperature glass at 77 K, the values are τ_D^0 = 50.5 ± 0.5 ns for polymer and 52.8 ± 0.5 ns for PhMP. The good agreement suggests that the polymer is free from both self-quenching and intramolecular excimer formation.[24] The donor (PhMMA) fluorescence decay curves were identical in poly(PhMMA–MMA) when viewed at 350 and 365 nm. Figure 1 shows decay curves at varying AMMA content. In fluid solution, the deviation of the fluorescence decays from exponentiality becomes increasingly more pronounced with increasing AMMA mole fraction, f_{AMMA}. Since no significant changes in the emission spectra were observed before and after the transient measurements, photochemical changes of the polymers can be ignored in interpreting the decay profiles. Fluorescence decay curves of PhMMA of the same copolymers measured at 77 K in 2MTHF/THF glass are shown in Figure 2.

Figure 3 shows the rate constant $k_m(\infty)$ vs. f_{AMMA} for the copolymers in fluid solutions (curve a). The method for determining $k_m(\infty)$ from the decay curves is explained in the Appendix. The linear dependence of $k_m(\infty)$ on f_{AMMA} is strong evidence that excitation mobility is exponen-

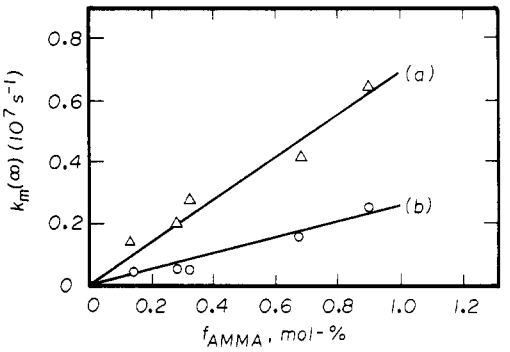

Figure 3. Long-time transfer rate, $k_m(\infty)$, of poly(PhMMA–AMMA): (a) in THF at 25 °C; (b) in 2MTHF/THF glass at 77 K. λ_{ex} = 280 nm, λ_{em} = 266 nm.

tialized the long-time region of the decay curves. If one considers the three theoretical models described earlier, it seems that the intermediate kinetic model best describes the decay of donor fluorescence for these polymers. However, the relative contributions of both segmental diffusion of the chain and energy migration of the excitation among the donors cannot be distinguished in experiments in fluid solutions.

The effect of segment mobility can be probed by studying the decay in hydrocarbon glasses at 77 K. Here, the deviation from exponentiality is less substantial than in the corresponding fluid solution measurements. This is probably due to the reduced dynamical single-step rapid transfer assisted with intrachain segmental diffusion. Even though the chromophores are practically stationary in the rigid glass at this temperature, a linear dependence of $k_m(\infty)$ on f_{AMMA} with a finite slope was observed and is shown in Figure 3 (curve b). The linear dependence of $k_m(\infty)$ on f_{AMMA} again demonstrates that the donor excitations are mobile, even in the absence of mass diffusion. According to the theoretical models discussed earlier, the slope of a $k_m(\infty)$ vs. acceptor concentration C_A plot measures the mobility (diffusion or migration) of the donor excitation. It is then clear that in these copolymers, the donor energy migration is solely responsible for the observed mobility at low temperature. In the fluid solutions, it is a combination of both energy migration and segmental diffusion which gives rise to the enhanced mobility. The two effects are not expected to be additive since segmental diffusion enhances the single-step transfer to the acceptor as well as intermediate migratory transfers. Furthermore, the singlet energy migration at low temperature, as measured by the slope of the $k_m(\infty)$ vs. f_{AMMA} plot, is comparable to the contribution from segmental diffusion.

According to the random walk model by Artamonova et al.,[34] the migration coefficient depends strongly on the concentration of the donor. This dependence therefore provides a further test of the proposed mechanism of singlet energy migration within the chain.

The introduction of the MMA comonomer in both the PhMMA–MMA copolymers and PhMMA–MMA–AMMA terpolymers has the effect of increasing the D → D distance in the polymer coil. This was studied on the absorption and emission characteristics of both the phenanthrene and anthracene chromophores. Table I gives the molecular weights and compositions of these polymers. The transient fluorescence decay curves of PhMMA in poly(PhMMA–MMA) were found to be single exponential, both in fluid solution and at 77 K in rigid glass. The decay rate $(\tau_D^0)^{-1}$ at 77 K varies only slightly over the whole range of copolymer compositions, as shown in Figure 4. In view of the absence of self-quenching in the homopolymer, the

Table I
Compositions and Molecular Weights of Poly(PhMMA-MMA-AMMA)

monomer feed ratio, mol % PhMMA: MMA:AMMA	polymer composition, mol % PhMMA: MMA:AMMA	$\bar{M}_n \times 10^{-5}$ [a]
3.06:96.74:0.20	3.54:96.37:0.09	0.89
3.38:96.27:0.33	2.37:97.35:0.25	4.34
3.18:96.40:0.42	4.71:94.63:0.66	6.50
3.37:95.98:0.64	2.64:96.49:0.87	3.12
3.47:95.67:0.86	3.49:95.24:1.27	6.40
6.11:92.88:1.01	10.60:87.77:1.63	6.10
41.88:57.08:1.04	58.44:40.07:1.49	6.75
45.29:53.56:1.15	75.48:22.88:1.64	5.70

[a] Membrane osmometry.

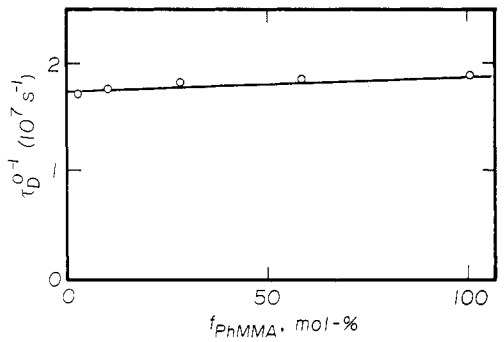

Figure 4. Variation of fluorescence decay rate $(\tau_D^0)^{-1}$ of poly(PhMMA-MMA) with f_{PhMMA} in 2MTHF/THF glass at 77 K. λ_{ex} = 280 nm, λ_{em} = 366 nm.

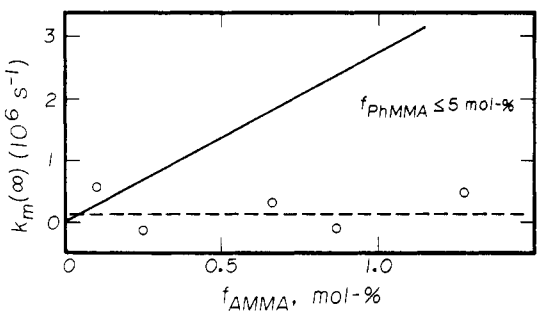

Figure 5. Long-time transfer rate, $k_m(\infty)$, of poly(PhMMA-MMA-AMMA) in 2MTHF/THF glass at 77 K vs. f_{AMMA}. λ_{ex} = 280 nm, λ_{em} = 366 nm. The solid line is curve b in Figure 3, shown for comparison.

slight variation of τ_D^0 here is attributed to the perturbation of the nonradiative decay of the phenanthrene excited state by the neighboring MMA units. At the same temperature, the D* fluorescence decays in the terpolymers with AMMA were found to be nonexponential. In the case where the donor content (f_{PhMMA}) is reduced to less than 5 mol %, energy migration among the donors is expected to be negligible. Figure 5 shows the $k_m(\infty)$ vs. f_{AMMA} plots for these low-donor-content polymers. The $k_m(\infty)$ values were found to be practically zero, independent of f_{AMMA} within experimental error. According to the prediction of Förster kinetics, the transfer in these polymers is primarily single-step direct transfer from phenanthrene to anthracene. This is strong confirmation of the interpretation of the earlier observations invoking singlet energy migration in polymers containing higher concentrations of donor. Increasing the donor content resulted in increasing $k_m(\infty)$ for a given AMMA concentration, as can be seen in Figure 6. This further substantiates the donor concentration dependence of energy migration predicted by the Artamonova model (eq 14 and 15) as well as other theories.[17,36]

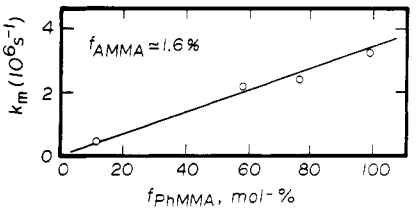

Figure 6. Long-time transfer rate, $k_m(\infty)$, of poly(PhMMA-MMA-AMMA) in 2MTHF/THF glass at 77 K vs. f_{PhMMA}.

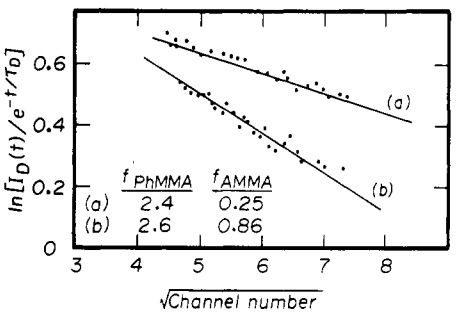

Figure 7. Short-time donor fluorescence decay of poly(PhMMA-MMA-AMMA) in 2MTHF/THF glass at 77 K. λ_{ex} = 280 nm, λ_{em} = 366 nm, time scale = 1.59 ns/channel.

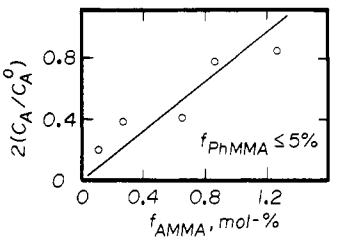

Figure 8. Effective acceptor (AMMA) concentration of poly(PhMMA-MMA-AMMA) in 2MTHF/THF glass at 77 K.

The remarkable correlation between the prediction of a simple theory and the experimental findings suggests that it can be applied to quantify the migration coefficient via eq 14. In order to do this, it is mandatory to relate the bulk acceptor concentration C_A in the theory to f_{AMMA} in the polymers.

In a dilute polymer solution, the net bulk concentration of AMMA and the effective local concentration are very different. The definition of local concentration, on the other hand, depends strongly on the type of reaction in which the species is involved. In this experiment, the relevant process is the dipole–dipole Förster energy transfer and hence C_A will be determined by this process. In the case of only single-step transfer between stationary donor and acceptor, Förster kinetics is obeyed and eq 1 and 2 can be rewritten as

$$\ln [I_{D^*}(t)/\exp(-t/\tau_D^0)] = (\text{const}) - 2(C_A/C_A^0)(t/\tau_D^0)^{1/2} \quad (16)$$

A straight-line plot of the left-hand side of eq 16 vs. $(t/\tau_D^0)^{1/2}$ gives a slope equal to $-2C_A/C_A^0$. Figure 7 shows typical plots of ln $[I_{D^*}(t)/\exp(-t/\tau_D^0)]$ vs. $t^{1/2}$ for two terpolymer samples for the short-time portion of the decay curves at 77 K. A linear relationship was observed in all the samples and the correlation between $2(C_A/C_A^0)$ and f_{AMMA} was observed to be approximately linear, as shown in Figure 8.

A first estimate of the degree of singlet energy migration among phenanthrene donor units in the polymer can be made. Using the approximate value for the critical transfer radius from phenanthrene to anthracene as 25.5 Å[37] and setting τ_D^0 = 52.8 ns as observed, one can then estimate

the migration coefficient in eq 14 to be $\Lambda \simeq 1.5 \times 10^{-5}$ cm^2/s. The migration length, defined by $\bar{l} \simeq (2\Lambda\tau_D^0)^{1/2}$, is estimated to be ca. 120 Å.

One may now estimate the effective range of transfer from phenanthrene to anthracene in the presence of energy migration. Approximating the rate of transfer $k_m(t)$ by $k_m(\infty)$ as given in eq 14, one obtains for the transfer efficiency

$$\chi \simeq \frac{k_m(\infty)\tau_D^0}{1 + k_m(\infty)\tau_D^0} \tag{17}$$

By making the same estimates for Λ, τ_D^0, and R_0 as before, one finds the effective bulk acceptor concentration C_A(eff) which would yield $\chi = 0.76$ to be ca. 2.38×10^{18} molecule/cm^3. This is equivalent to an effective Förster radius of R_0(eff) = 48.4 Å from phenanthrene to anthracene. Note that R_0(eff) = 48.4 Å would be a lower estimate since $k_m(\infty)$ used in eq 16 did not take into account the transfer due to single-step direct transfer occurring at short time.

Conclusions

The donor fluorescence decay technique employed here makes possible the quantification of the extent of singlet energy migration in phenanthrene-containing polymers. The technique is sensitive to the migration process, even when the rate is lower than that of small-molecule diffusion in nonviscous media. The good fit between the experimental results and the predictions of the Artamonova model, as expressed in eq 13–15, suggests that the inhomogeneity of the spatial distribution of the chromophores bound on the polymer as well as the finite spatial extension of the polymer coil may not be a critical factor in determining the overall donor fluorescence decay behavior.

The transfer of singlet energy from the donors to the small proportion of bound acceptors in PhMMA–AMMA co- and terpolymers is primarily through energy migration followed by a one-step downhill transfer to the trap in a solid medium. In fluid solutions, segmental diffusion enhances the rate of both migration and single-step transfer and subsequently improves the overall transfer rate and efficiency. These observations have important implications on the design of polymeric molecular antenna systems for efficient harvesting of solar energy.

Acknowledgment. We gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada for financial support of this research and for fellowship support to D.N. Thanks are extended to Dr. D. A. Holden and Dr. J. R. MacCallum for valuable discussions.

Appendix. Curve-Fitting Procedure

Experimentally, the quantity $k_m(t)$ is determined by the relation

$$k_m(t) = (1/\tau_D)_{exptl}(t) - 1/\tau_D^0$$

where $(1/\tau_D)_{exptl}(t)$ is the experimentally determined time-dependent decay rate of the donor fluorescence and τ_D^0 is the unperturbed decay lifetime of D* at the corresponding PhMMA/MMA ratio in the polymer chain in the absence of the acceptor. Since information on energy migration (or diffusion) rate is drawn only from the long-time asymptotic decay, $(1/\tau_D)_{exptl}(t = \infty)$ is the quantity of interest.

If the fluorescence decay obeys strict Stern–Volmer kinetics with a best-fit lifetime τ, then $(1/\tau_D)_{exptl}(\infty) = 1/\tau$. In the other two regimes, $(1/\tau_D)_{exptl}(\infty)$ is determined by the longest best-fit relaxation time ($\equiv\tau_{max}$) from a multiexponential fit. In the present studies, biexponential fits ($\tau_{max} = \tau_2$) and triexponential fits ($\tau_{max} = \tau_3$) were employed.

Several criteria were imposed on the validity of the assignment of $(1/\tau_D)_{exptl}(\infty)$. The reduced χ^2 value of a particular fit will serve as the general guideline for quality of fit. A given nonexponential decay curve will be fitted with a biexponential fitting program but the starting channel of fit will be varied to ensure that τ_{max} ($=\tau_2$) is not sensitive to this variation. A stable τ_{max} would imply that τ_{max} so obtained measures the asymptotic exponential decay time. If these conditions are not satisfied, a similar procedure is taken using a triexponential fitting program.

In the authors' experiments, a reliable τ_{max} is usually obtained with the biexponential fitting procedure. Occasionally, decay measurements were repeated at time scales about 2 times that of the original experiment to ensure the asymptotic exponential region was attained.

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