1034 *Macromolecules* 1985, *18*, 1034–1039

support in most studies in inverse gas chromatography. This material seems to contain small amounts of polymeric materials, most probably poly(dimethylsiloxane) (PDMS), which interacts with most chromatographic probes. In addition, the support has a small number of highly polar surface groups (probably hydroxyls) which interact strongly with polar groups. PDMS retains most probes, making a constant contribution to retention volume. The polar groups retain only the polar probes, making a very large contribution to the retention volume at very small injections, and having a smaller effect at large injections. The retention characteristics of the support are preserved even when columns are coated with polymers. To obtain meaningful data for the retention volume V_g of various probes on polymer (and for the thermodynamic quantities derived from them), it is necessary to subtract the contribution to V_g that is caused by the support from the overall retention volume. Using this procedure for polyisobutylene and several polar and nonpolar probes, we obtained V_g values that were independent of the amount of probe injected, polymer loading, and flow rate. This method seems also to apply to the more polar polymer, poly(methyl acrylate). Using the correction procedure is particularly important for both polar probes and for polymer–probe pairs that interact only sparingly.

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Energy Migration in the Aromatic Vinyl Polymers. 4. Blends of Poly(2-vinylnaphthalene) with Poly(cyclohexyl methacrylate)

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ABSTRACT: A significant problem in the modeling of photostationary excimer fluorescence of blends of aryl vinyl polymers is the need for data on the various photophysical parameters for these models. One parameter of general importance is the ratio of the intrinsic quantum yields of the excimer to the monomer, Q_e/Q_m. In this work a photophysical model and experimental technique are developed that allow the determination of Q_e/Q_m. In order to apply this method, the host matrix must be miscible with the guest fluorescent polymer at low concentrations and a suitable small probe molecule must be available to model the polymer monomer signal. Solvent-cast films containing 0.1–1.0 wt % poly(2-vinylnaphthalene) (P2VN) and 0.0–2.0 wt % 2-ethylnaphthalene in poly(cyclohexyl methacrylate) (PCMA) were prepared and studied by using photostationary excimer fluorescence. Two major results were obtained from the application of the model to the data. First, Q_e/Q_m for P2VN dispersed in PCMA was found to be 0.44 ± 0.08. Second, the ratio of the rate of nearest-neighbor energy transport to the monomer decay rate was found to be 1 order of magnitude larger for P2VN than for polystyrene.

Introduction

In a recent series of papers, excimer fluorescence has been used as a molecular probe of the thermodynamics of polymer blends.[1-5] Despite the success of the rather phenomenological approach employed in the early work, a detailed understanding of the photophysics of these

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systems has proved elusive. The important experimental parameter in the photostationary-state experiments generally performed is the ratio of integrated excimer to monomer fluorescence intensities, Φ_e/Φ_m. In the first paper of the present series on energy migration in aromatic vinyl polymers,[6] it was shown that this quantity may be related to the relevant photophysical parameters by

$$R = \frac{\Phi_e}{\Phi_m} = \frac{Q_e}{Q_m}\left[\frac{1-M}{M}\right] \tag{1}$$

where R = ratio of integrated areas of excimer (Φ_e) to monomer (Φ_m) fluorescence, Q_e = intrinsic quantum yield of excimer, Q_m = intrinsic quantum yield of monomer, and M = probability of eventual excitation dissipation by radiative or nonradiative paths from a monomer site.

Although eq 1 does not presuppose a specific photophysical model, Q_e/Q_m is assumed to be independent of concentration, but not necessarily of temperature, for a given polymer blend. Note that in earlier work Q_e/Q_m was denoted as Q_d/Q_m.[6] In general, M is a complex function of polymer concentration, molecular weight, and temperature. Regardless of the model used to develop an expression for M, Q_e/Q_m must be known in order to use eq 1 to analyze quantitatively the fluorescence of polymer blends.

In a recent review, it was proposed that an average value of Q_e/Q_m determined in various solvents could be used for polymer films.[7] This assumes, however, that Q_e/Q_m is independent of both the chemical interactions as well as the fluidity of the host matrix. Although Q_e and Q_m seem to be independent of solvent for the aryl vinyl polymers, polar solvents do lead to higher values of Q_e/Q_m.[7] In addition, a slight matrix dependence has been found for the poly(naphthylalkyl methacrylates).[8] Moreover, there does not seem to have been any study of the influence of fluidity in liquid and solid matrices of similar chemical composition.

In view of the possible errors associated with the use of solution values for Q_e/Q_m, we have developed an experimental approach to the determination of Q_e/Q_m in a solid-state blend. The method requires that the blend be miscible at low concentration of the fluorescent polymer. Then a suitable small molecule that accurately models the fluorescence of the polymer monomer is dispersed in the blend. As will be shown, this approach has the advantage of requiring only photostationary-state measurements of the ratio of net quantum yields of excimer and monomer.

Photophysical Model

Before we describe the proposed model, it is of interest to outline previous approaches for the determination of Q_e/Q_m. In the first method, which is based upon the early work of Hirayama and Lipsky,[9] it is noted that

$$\Phi_e/Q_e + \Phi_m/Q_m = 1 \tag{2}$$

where Φ_e and Φ_m are the net quantum yields of excimer and monomer. Two experimental approaches have commonly been taken for application of eq 2.[9,10] In the first, Φ_e and Φ_m are measured in a series of solvents. Then, if Q_e and Q_m *are independent of solvent, a plot of* Φ_e vs. Φ_m will yield Q_e and Q_m. Alternatively, Φ_e and Φ_m may be measured as a function of polymer molecular weight. If Q_e and Q_m are independent of molecular weight, a plot of Φ_e vs. Φ_m will also yield Q_e and Q_m.

The principal barrier to this type of approach in polymer films is that it is difficult to measure the net quantum yields. This is primarily because it is difficult to make films of exactly the same thickness, reproducibly. Thus, the optical path length is generally not well-defined. In addition, although front-face illumination must be used to minimize self-absorption, the depth of penetration of the excitation light is not exactly known.

An alternative method of measuring Q_e/Q_m in films relies on a scheme developed by Hirayama[10] for bichromophoric model compounds. This technique is also applicable to polymeric systems in rigid matrix. In this approach, eq 1 is broken up into two equations.

$$\Phi_e = Q_e(1 - M) \tag{3}$$

$$\Phi_m = Q_m(M) \tag{4}$$

Note that eq 4 will be true only if the excimer does not dissociate to excited monomer; such an assumption has been shown to be valid for P2VN.[6] The difficulty with using eq 3 and 4 to solve for Q_e and Q_m is that there are two equations with three unknowns. Hirayama solved this problem by noting that Φ_0, the net quantum yield for a monochromophoric model compound that contains the same chromophore as the polymer, is equal to Q_m under certain conditions. The conditions are that the film or solution of the model compound should be dilute enough so that excimer formation may be neglected. Furthermore, the monochromophoric model compound film and the polymer film must have identical chromophore concentrations. If these conditions are met, then

$$\Phi_0 = Q_m \tag{5}$$

Combining eq 3–5 we obtain

$$Q_e/Q_m = \Phi_e/(\Phi_0 - \Phi_m) \tag{6}$$

Unfortunately, this scheme also suffers from difficulties in accurately determining net quantum yields for films.

In their study of poly(naphthylalkyl methacrylate) copolymers, Holden and Guillet[11] obtained net quantum yields by using the approximate relation

$$\Phi_{\text{ref}}/\Phi_{\text{film}} = \tau_{\text{ref}}/\tau_{\text{film}} \tag{7}$$

where Φ_{ref} and Φ_{film} refer to data from a reference solution and from a film, respectively; τ_{ref} and τ_{film} are the corresponding decay times. Since this method requires the use of transient fluorescence techniques, which are not always available, it would be convenient to develop a technique that relies only on photostationary measurements.

The photophysical scheme for the model compound–polymer blend system is based upon several requirements and assumptions. The requirements are, first, that the guest polymer concentration be in the dilute regime, second, that the blend be miscible, and, third, that the model compound be uniformly distributed in the blend.

Under these conditions we may assume that the guest polymer coils are isolated and that small changes in the guest polymer concentration should not appreciably increase the number of interchain contacts. Moreover, for sufficiently low model compound concentrations, excimer-forming sites will be formed only in the polymer but not among the molecules of the model compound. For the same reason, we expect that energy migration will take place between the model and the polymer and within the polymer coil but not among the model compound rings. From the similarity of the model compound and monomer spectra we assume that the quantum yields are identical. Finally, we assume that the excimer-forming sites form nondissociative traps which do not permit transfer or crossing from excimer to monomer.

The system requirements suggest that M is a constant. This assumption of constant M will be valid as long as R remains constant while the guest polymer concentration is varied, in the absence of model compound. To calculate

R we start with simple probabilistic arguments

$$R = \frac{Q_e}{Q_m}\frac{P_e}{P_m} \tag{8}$$

where P_e, P_m = probability of excimer or monomer decay. Furthermore, we find that

$$P_e = f_p(1 - M) + f_{mm}A(1 - M) \tag{9}$$

$$P_m = f_pM + f_{mm}AM + f_{mm}(1 - A) \tag{10}$$

where f_p = fraction of rings in polymer, i.e., $f_p = f_e + f_{mp}$, f_e = fraction of rings in excimer-forming sites (EFS) based upon the total number of rings in the system including both polymer and model compound, f_{mp} = fraction of rings in monomer sites on the polymer, f_{mm} = fraction of rings in model compound, and A = probability of eventual transfer from model to polymer. Combination of eq 8–10 leads to

$$R = \frac{Q_e}{Q_m}\left[\frac{(1 + \beta A)(1 - M)}{M + \beta[1 - A(1 - M)]}\right] \tag{11}$$

where

$$\beta = f_{mm}/f_p$$

To derive an expression for A, we require the time-dependent probability that an excitation created on a model ring at time zero still resides on the same ring at a later time t. This probability will be designated $G^s(t)$, and it is related to A by

$$A = 1 - \frac{\int_0^\infty \mathrm{d}t\, G^s(t)e^{-k_mt}}{\int_0^\infty \mathrm{d}t\, e^{-k_mt}} \tag{12}$$

where k_m is the inverse of the measured lifetime of an excitation on an isolated model ring. If the Laplace transform is defined by

$$\hat{G}^s(\epsilon) = \int_0^\infty \mathrm{d}t\, G^s(t)e^{-\epsilon t} \tag{13}$$

eq 12 can be written

$$A = 1 - k_m\hat{G}^s(k_m) \tag{14}$$

An approximation to $\hat{G}^s(\epsilon)$ can be obtained by assuming isotropic Förster transport and by neglecting excitation transfer between model rings, which are present at low concentration. Furthermore, the model rings and guest polymer molecules are assumed to be randomly distributed in the host matrix. Under these conditions, the two-particle Padé approximant for $\hat{G}^s(\epsilon)$ takes the form[12,13]

$$\hat{G}^s(\epsilon) = \epsilon^{-1}\left[1 + \pi\left[\frac{C_{mp}}{2^{3/2}} + \frac{C_e}{2}\right]\frac{k_m}{\epsilon}\right]^{-1} \tag{15}$$

where C_{mp} and C_e are dimensionless concentrations of monomeric and excimeric rings on the polymer

$$C_{mp} = \rho\frac{4}{3}\pi R_0^3N\frac{f_{mp}}{f_p}$$

$$C_e = \rho\frac{4}{3}\pi R_0^3N\frac{f_e}{f_p} \tag{16}$$

where R_0 is the Förster radius for transfer between model and polymer rings, N is the average number of chromophores per chain, and ρ is the number density of guest polymer molecules. Equation 15 is exact to first order in the dimensionless concentrations, and it is well-behaved at long times and higher concentrations. Combining eq 14 and 15, we obtain

$$A = \alpha\rho/(1 + \alpha\rho) \tag{17}$$

where

$$\alpha = \frac{4}{3}\pi^2R_0^3\frac{N}{f_p}\left[\frac{f_{mp}}{2^{3/2}} + \frac{f_e}{2}\right] \tag{18}$$

At this point, it is apparent from eq 11 and 17 that use of experimentally specified values of β and ρ along with measured values of R leads to a three-parameter model in the unknowns Q_e/Q_m, M, and α. This model may be simplified for the case where the polymer and the model compound concentrations are low. If this is true, we may neglect transfer from the model to the polymer; hence, $A \ll 1$. Furthermore, if detailed information about the one-dimensional energy transport is not desired, then M may be treated as a simple constant. Under these conditions eq 11 reduces to a two-parameter fit

$$R = \left[\frac{Q_e}{Q_m}\right]\left[\frac{1 - M}{M + \beta}\right] \tag{19}$$

In order to characterize the energy-transport process, it is necessary as a final task to develop an analytical expression for M. We will present the results of two different modeling efforts. In the first treatment, from arguments based upon the statistics of a one-dimensional random walk on a polymer chain in the limit of infinite molecular weight, M is given by[6,14]

$$M = 1 - q_d - \frac{q_d^2}{\tanh\theta}\sum_{x=1}^{\infty}(1 - q_d)^x \tanh(\theta x) \tag{20}$$

$$\theta = \frac{1}{2}\ln\left[\frac{1 + 2E + (1 + 4E)^{1/2}}{2E}\right] \tag{21}$$

where $q_d = f_e/2f_p$ and $E = W/k_m$. W is the one-dimensional nearest-neighbor transport rate and k_m is the monomer decay rate.

A second, more recent, and exact solution to the one-dimensional, nearest-neighbor transport and trapping problem is given by Movaghar[15]

$$M = \frac{f_{mp}}{f_p}\left[\sum_{n=0}^{\infty}\frac{q_d^2(-1)^nh^{2n}(1 - h)^2}{[1 - (1 - q_d)h^n]^2[1 - (1 - q_d)h^{n+1}]^2}\right] \tag{22}$$

where

$$h = g/(g + 1)$$

$$g = [(1 + 4E)^{1/2} - 1]/2 \tag{23}$$

If detailed information about the one-dimensional transport process in the polymer is desired, then either of the models could be used to calculate M. Since each of these relations for M contains two unknowns, f_e/f_{mp} and W, one of these quantities must be fixed and the other used as a fitting parameter. The method of doing this is described in the Results and Discussion section.

Experimental Section

The P2VN was a polydisperse sample prepared and purified by Gashgari[4] with a molecular weight peak at 71 000 as determined by GPC.[16] The poly(cyclohexyl methacrylate) (PCMA) and 2-ethylnaphthalene (2-EN) were obtained from Aldrich Chemical Co. and used as received. The toluene is Burdick and Jackson "distilled-in-glass" grade.

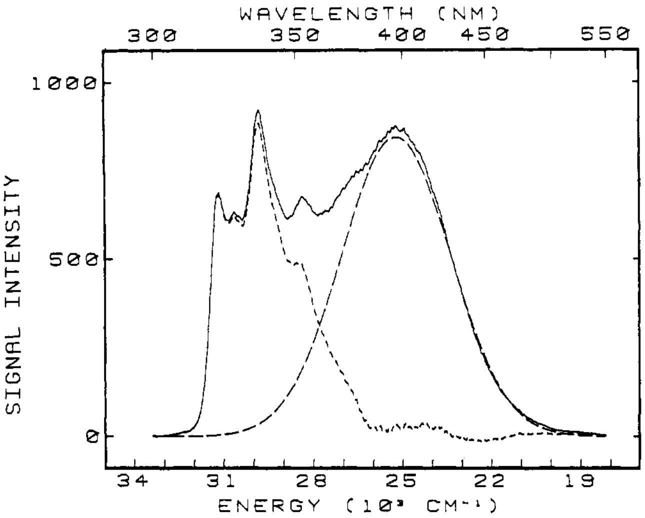

Figure 1. Typical corrected spectrum of P2VN mixed with 2-EN in the PCMA host. Both the structured monomer envelope and the unstructured excimer envelope are shown with dashed lines.

The films were prepared by making approximately 1-mL toluene solutions containing a total of 30 mg of polymer and the desired ratio of 2-EN to P2VN. The solution was then allowed to dry on a microscope slide using a surface area of 1 in. × 2 in. Care was taken in the selection of microscope slides since it was found that their fluorescence varied considerably from box to box, and manufacturer to manufacturer.[17] In general, the integrated signal of the intrinsic slide fluorescence was about 1% of the signal from the sample fluorescence.

One experimental requirement with films prepared by solvent casting is that the model compound should be as nonvolatile as possible so that the dried film contains the desired amount of model compound. Since the boiling point of the casting solvent is 110.6 °C, all of the films were dried for only 1 day and the spectra promptly taken. With these precautions the loss of 2-EN was considered negligible.

After the films were allowed to dry overnight at room temperature, three spectra were taken from different portions of each film sample. The excitation wavelength was 290 nm. Front-face illumination spectra were taken in air, at room temperature, on a spectrofluorimeter that has been described elsewhere.[2] The data were collected and stored on a PDP 11/23 minicomputer. A spectral correction for the instrument response was applied, and integrated areas for the monomer and excimer were calculated by using programs adapted from the work of Fitzgibbon.[18]

Results and Discussion

There are four sets of data in this study. In three of them the P2VN concentration is held constant at either 0.15, 0.30, or 1.0 wt % where β is varied from 0.0 to 2.0. In the fourth data set the P2VN concentration is varied from 0.1 to 1.0 wt % while β is held constant at 1.0. We will begin by discussing the first group of three data sets. A typical spectrum is shown in Figure 1. Both the monomer (structured high-energy emission) and excimer (structureless low-energy emission) envelopes are shown.

PCMA was chosen as the host matrix because excimer fluorescence experiments have shown it to be one of the most compatible poly(alkyl methacrylates) with P2VN.[5,19] In a separate study, blends were prepared over the complete concentration range of P2VN and PCMA. All of these films were clear when cast from toluene. Furthermore, the excimer fluorescence showed no abrupt change with concentration that would suggest phase separation. The question of the miscibility of the P2VN/PCMA blend will receive detailed treatment in a future paper.[20]

The average value of R among the different data sets when $\beta = 0$ is 1.59 ± 0.10, which is constant within experimental error. This is important, since it helps to establish the fact that M is not varying appreciably for the three different concentrations of P2VN. Other experiments have shown that R starts to increase with concentration once the concentration of P2VN in PCMA is beyond about 1%.[20] This is good agreement with the fact that C^*, the concentration that marks the transition from the dilute to semidilute regime, is about 2.5 wt % P2VN.

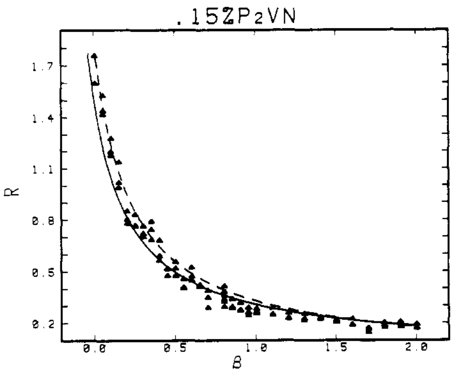

Figure 2. Comparison of fluorescence data with the best fits of the three-parameter (solid line) and two-parameter (dashed line) models. The concentration of P2VN is held constant at 0.15 wt %. See the text for the definition of β.

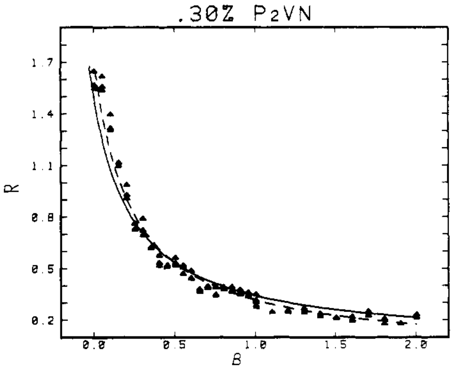

Figure 3. Comparison of fluorescence data with the best fits of the three-parameter (solid line) and two-parameter (dashed line) models. The concentration of P2VN is held constant at 0.30 wt %.

The three-parameter model was fitted to the entire collection of data for this blend, which contains a total of almost 300 data points. The least-squares fitting program that was used has a provision that allows for the initial guesses to be randomly perturbed values of the previous best fit. In this way the uniqueness of the solution can be tested. Once a good general best fit was found, the parameters were randomly perturbed by a maximum of ±50% and then used as initial guesses for a new iteration cycle. After 20 such iteration cycles the best fit was found to be

$$Q_e/Q_m = 0.44 \pm 0.08$$

$$M = 0.22 \pm 0.02$$

$$\alpha = 0.56 \pm 0.12$$

$$\chi^2 = 9.4 \pm 10^{-4}$$

where

$$\chi^2 = \frac{\sum(R_{\text{exptl}} - R_{\text{fit}})^2}{\text{degrees of freedom}}$$

and ρ is expressed as the weight percent of P2VN. These results are shown in Figures 2–5 with the solid line representing the fitted curve for the three-parameter model.

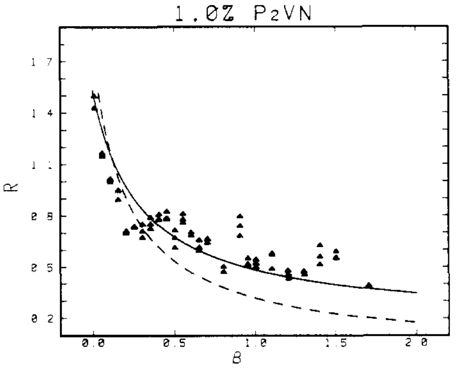

Figure 4. Comparison of fluorescence data with the best fits of the three-parameter (solid line) and two-parameter (dashed line) models. The concentration of P2VN is held constant at 1.0 wt %.

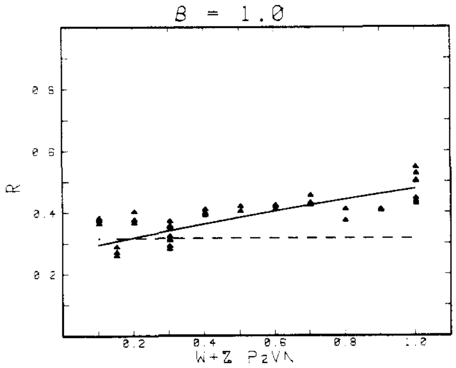

Figure 5. Comparison of fluorescence data with the three-parameter model (solid line) and the two-parameter model (dashed line). β is held constant at 1.0.

If the 0.15 and 0.30 wt % data are fitted to the two-parameter model, the results are

$$Q_e/Q_m = 0.50 \pm 0.05$$

$$M = 0.22 \pm 0.02$$

$$\chi^2 = 3.17 \times 10^{-1}$$

The fit is shown in Figures 2–5 as a dashed line. χ^2, which is a measure of the goodness of fit, is much larger for the two-parameter model; furthermore, the 1.0 wt % data are not fitted very well with the two-parameter model. This is not at all surprising since the 1 wt % P2VN films are approaching the semidilute regime. Because of this, many of the 2-EN molecules will be close enough to a polymer molecule to allow single-step energy transport to the polymer. These results show the need for using the three-parameter model for all but very dilute cases.

Semerak has performed an extensive literature survey of the fluorescence of various naphthalene-based model compounds in solution[7] in which he found $Q_e/Q_m = 0.55 \pm 0.15$. Although the difference between this average solution value and the present result of 0.44 ± 0.08 for the three-parameter fit is only modest, the most accurate work for future studies with polymer blends would still warrant use of the model compound approach.

Equation 18 can be used to calculate a value of R_0 from α, which will serve as a check on the accuracy of the α value. Since ρ was in units of wt % P2VN, care must be taken to convert α to the proper units of Å^3/(number of molecules) in order to use eq 18. If we assume that R_0 is the same for the model, monomer and excimer, then $R_0 = 11.75$ Å[19]. The result is $\alpha_{\text{calcd}} = 0.33$ while $\alpha_{\text{exptl}} = 0.56 \pm 0.12$. The agreement between experiment and theory is good. The fact that α_{calcd} is less than α_{exptl} implies that the real transfer rate from the model to the polymer is somewhat higher than the theory would predict. A close inspection of eq 18 shows that α is not very sensitive to changes in f_e, since $f_e/f_p + f_{mp}/f_p = 1$. Although the difference between α_{calcd} and α_{exptl} could be accounted for by a 12% increase in R_0, this is not considered likely. The most likely cause for the difference between experiment and theory is that the model compound may not be uniformly distributed. If the model compound preferred the guest polymer, then this could account for the increase in α for the experimental case.

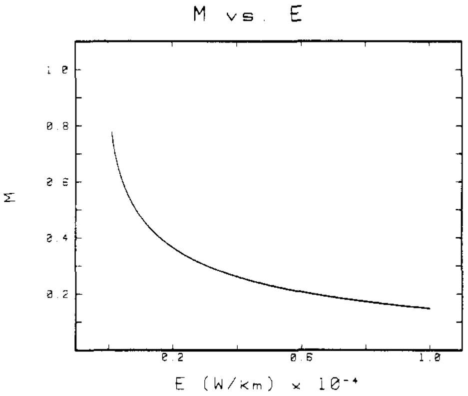

Figure 6. Comparison of the two different models for the dependence of M on E, for a given $f_e/f_m = 0.027$. The two models are superimposable, within the accuracy of the plot.

The final point of interest is to calculate E, the ratio of the rates of one-dimensional transport, W, to monomer decay, k_m, by using the relations in eq 20 and 22. Each of these methods of calculating M has two unknowns, W and f_e/f_{mp}. Since f_e/f_{mp} can be calculated from conformational statistics, it is then straightforward to determine W and, hence, E.

A similar problem has been solved for polystyrene (PS).[22] Since a detailed conformational calculation for P2VN would require tacticity information, which we do not have, and since the energy maps for bichromophoric models of P2VN are very similar to PS,[23] we will use the results of the PS calculation.[16] The only difference is that the tt-meso dyad, which is the dominant EFS, has one more degree of freedom in the P2VN as compared to PS. The naphthyl rings in P2VN may rotate and assume two different positions, one of which is an EFS, the other of which is not.[7] Assuming equal probability for these events, we arrive at a value of $f_e/f_{mp} = 0.027$.[16]

The dependence of M on E, using this value of f_e/f_{mp}, is shown in Figure 6. Both eq 20 and 22 yield the same results, to within a few percent. However, eq 20 takes about 1 order of magnitude more terms to converge, and much more computer time than eq 22. From the value of $M = 0.22$ determined earlier, we find from Figure 6 that $E = 5900 \pm 800$.

In the recent study of PS,[22] E was calculated by using the model of Fitzgibbon.[6] It was found that $E = 660$[16] for PS in poly(vinyl methyl ether). This is of interest since it shows that the relative rate of one-dimensional transport to monomer fluorescence is 1 order of magnitude larger for P2VN than for PS. Therefore, the exciton in P2VN is likely to sample many more sites during its one-dimensional random walk than an exciton in PS.

In summary, a straightforward experimental technique has been developed for determining the value of Q_e/Q_m for polymeric systems in the glassy amorphous state. In particular, a value of $Q_e/Q_m = 0.44 \pm 0.08$ was found for P2VN in PCMA. In light of the relatively small difference between this value for Q_e/Q_m and that estimated earlier,[7] it appears that the effect of the solid matrix is only small. A more important observation is that the ratio of the rate of one-dimensional transport to the monomer decay rate is 1 order of magnitude larger for P2VN than for PS in solid-state blends. This will be relevant to the analysis of the photophysics of P2VN and PS in solution. In such a case segmental motion could play a significant role in the overall excimer formation process if the rate of conformational change is comparable to the rate of the exciton migration among the chromophores.

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