a lower critical solution temperature.

Summary

The results demonstrate quantitatively that excimer fluorescence of isolated polymer chains dispersed in a rigid "solvent" of good quality can be analyzed in terms of a one-dimensional random walk in which transfer only to nearest neighbors is possible. Molecular weight and temperature effects have been explained in a consistent manner using the theory of random walks. The fluorescence results at temperatures greater than 303 K are consistent with a slight reduction in coil dimensions for isolated chains, leading to an increase in the dimensionality of the random walk.

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Energy Migration in the Aromatic Vinyl Polymers. 3. Three-Dimensional Migration in Polystyrene/Poly(vinyl methyl ether)

Richard Gelles and Curtis W. Frank*

Department of Chemical Engineering, Stanford University, Stanford, California 94305.
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ABSTRACT: A relatively simple three-dimensional energy migration model has been developed and used to explain the dependence of the ratio of excimer to monomer fluorescence on concentration for miscible polystyrene/poly(vinyl methyl ether) blends cast from toluene. The model is based on a lattice approach for the determination of the dependence of the rate of energy migration and the number of excimer-forming sites on concentration. It is applicable at concentrations for which the rate of off-chain transfer is equal to the rate of down-chain transfer. It has been found that, although singlet energy migration is important at high polystyrene concentrations, excitons make only a small number of hops before emission or trapping at an excimer-forming site. In addition, the experimental results for miscible blends have been utilized in a quantitative analysis of the concentration dependence of the ratio for immiscible blends cast from tetrahydrofuran. A two-phase model was applied, in which it is assumed that energy migration does not occur between the phases. The volume fractions of polystyrene in the rich and lean phases have been obtained from application of this model to the fluorescence data.

Introduction

Singlet energy migration in the aromatic vinyl polymers has been reviewed by Klöpffer[1,2] and found to be an important photophysical process. Recently, however, MacCallum has proposed that it does not take place in pure polystyrene films.[3,4] In the present work, the concentration dependence of the fluorescence of polystyrene dispersed in poly(vinyl methyl ether) has been studied in order to determine whether singlet energy migration occurs in concentrated polystyrene systems.

The mechanism of exciton hopping may be considered to be a series of single-step Förster transfers between aromatic chromophores.[5] For the case of low-concentration polystyrene/poly(vinyl methyl ether) blends, the presence

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of energy migration results in an efficient sampling of chromophores, leading to a larger ratio of excimer to monomer fluorescence than would be expected in the absence of migration.[6] This migration process may be viewed as a random walk of the electronic excitation. At each step in the walk, the excitation may be emitted from an isolated chromophore or monomer. Alternately, the excitation may be trapped at an excimer-forming site followed by excimer emission.

The problem of a random walk with emission and traps has been the subject of numerous analytical studies. Levinson treated a walk on an infinite one-dimensional lattice with emission and randomly placed traps.[7] This approach was extended to finite-length chains by Fitzgibbon[8] and has been used to study the fluorescence of isolated polymer chains.[6,8] Rosenstock investigated random walks in one, two, and three dimensions with traps at the boundaries[9] whereas Rudemo examined simple three-dimensional walks with randomly distributed traps.[10]

Much of the significant work dealing with random walks has been accomplished by Montroll, who has applied generating function techniques to walks on periodic lattices. This field of study has been reviewed by Barber.[11] One of the more important results has been the determination of the number of distinct sites visited in n steps as n approaches infinity for one-dimensional, two-dimensional, and different types of three-dimensional lattices. In a recent computer simulation study,[12] some of the earlier analytical results have been reproduced numerically. In this same work, hopping to all possible neighbors with a distance dependence corresponding to the Förster mechanism was also treated.

The PS/PVME blend is an ideal system for studying energy migration in polymers because its morphology is easily controlled by the method of preparation. For example, it has been shown from a number of experimental techniques that film casting from toluene leads to apparently miscible blends.[13-17] In paper 2 of this series[6] the molecular weight dependence of the ratio of excimer to monomer fluorescence of polystyrene (PS) dispersed at a low concentration in miscible blends with poly(vinyl methyl ether) (PVME) was quantitatively analyzed by using the one-dimensional random walk model of Fitzgibbon.[8] The purpose of this work is to study the effect of PS concentration on the fluorescence ratio for both miscible and immiscible systems. Because the PS/PVME blend is well characterized, the results should be more clear-cut than those from earlier studies dealing with systems for which little is known about the thermodynamics.[18-21]

Experimental Section

Polystyrene samples of molecular weights 4000 and 100 000 and polydispersities reported to be less than or equal to 1.06 were obtained from Pressure Chemical Co. They were purified by multiple precipitation from toluene into methanol. The PVME is the GAF Gantrez M-574 product, which has a molecular weight of 44 600 as determined from the intrinsic viscosity in benzene at 303 K and the Mark–Houwink constants of $K = 7.6 \times 10^{-4}$ and $a = 0.60$. Because of its low glass transition temperature, a special purification technique had to be developed for PVME. One gram of activated carbon (Norit) per gram of polymer was added to a 0.06 g/mL solution of PVME in toluene. These solutions were shaken vigorously for 3 days, after which the carbon was removed by filtration. This procedure reduced fluorescent impurities in the PVME by a factor of 10.

Solid films, 10 μm thick, were prepared by casting from toluene or tetrahydrofuran (THF) onto sapphire disks at room temperature. Those cast from toluene were then dried under vacuum at 323 K for at least 4 days to promote removal of the casting solvent. No evidence of residual solvent was found in the fluorescence spectra of pure PVME films prepared under identical conditions. Films cast from the more volatile THF were dried in air for only 12 h.

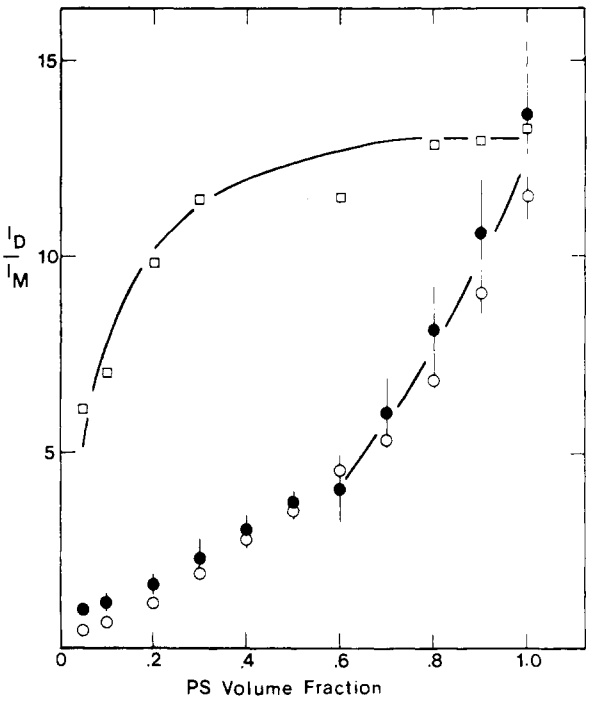

Figure 1. Comparison of experimental results for the concentration dependence of the ratio of excimer to monomer fluorescence intensities, I_D/I_M, for polystyrene (PS) in miscible PS/PVME blends with the best fit of the three-dimensional energy migration model: (○) miscible blend of PS of $\bar{M}_n$ = 4000 with PVME cast from toluene; (●) miscible blend of PS of $\bar{M}_n$ = 100 000 with PVME cast from toluene; (—) fit of the model. Also, comparison of experimental results for the concentration dependence of I_D/I_M for immiscible PS/PVME blends cast from THF using PS with $\bar{M}_n$ = 100 000 with the best fit using the two-phase model: (□) experimental data; (—) fit of the model.

Fluorescence spectra were taken in air at room temperature with a spectrofluorimeter that has been described earlier.[18] A front-face arrangement was used to minimize self-absorption and excitation was at 260 nm. Simple fluorescence intensities were measured at 280 nm (monomer) and 332 nm (excimer), where there is no overlap of excimer and monomer bands.

Results

As expected, all films cast from toluene were optically clear. The PS/PVME films cast from THF, however, were all extremely cloudy, indicating phase separation with domain sizes larger than the wavelength of visible light. An important observation is that the THF-cast films turned cloudy within the first few minutes of drying. Although THF is highly volatile, it appears that phase separation takes place in these films when there is still a significant amount of solvent present.

The dependence of the ratio of excimer to monomer fluorescence, $R \equiv I_D/I_M$, on polystyrene volume fraction for PS/PVME blends cast from toluene with PS molecular weights of 4000 and 100 000 is shown in Figure 1. At low concentrations, the ratio is larger for blends with the higher molecular weight polystyrene. As the PS concentration increases, however, the molecular weight effect diminishes until at a concentration of about 20–30%, the two ratios are the same within experimental error. In Figure 2, the percent difference between the two ratios is plotted as a function of PS volume fraction to amplify this point.

Figure 1 also shows the results for THF-cast blends made with polystyrene of molecular weight 100 000. At low concentrations, these films have much larger ratios

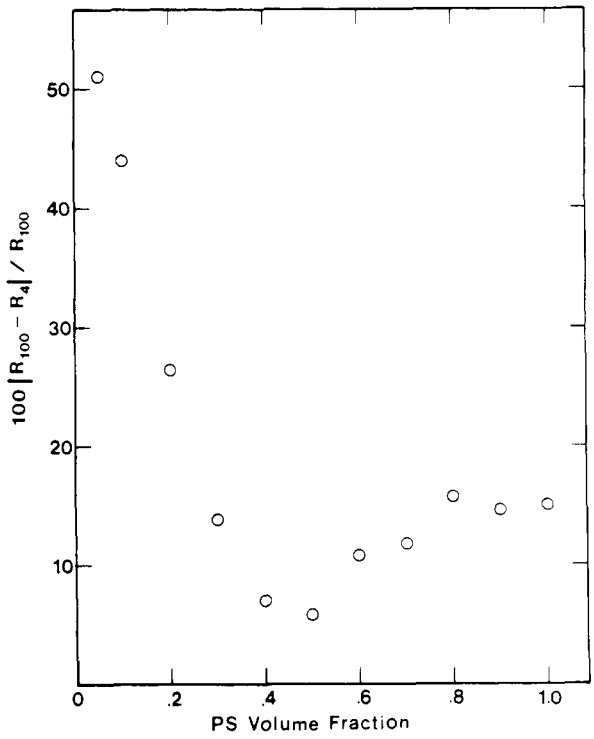

Figure 2. Percent deviation of the excimer to monomer fluorescence ratios between the PS samples of $\bar{M}_n$ = 100 000 and $\bar{M}_n$ = 4000 as a function of PS concentration in miscible blends cast from toluene.

than those cast from toluene. For PS concentrations greater than 30%, the THF-cast films have ratios essentially equal to that of pure polystyrene.

Discussion

A. Miscible Blends Cast from Toluene. At low PS concentrations, the ratio of excimer to monomer fluorescence for miscible (toluene cast) PS/PVME blends depends on the PS molecular weight. A detailed analysis of the molecular weight effect for isolated chains was given in the first two papers of this series.[6,8] For the case of isolated chains, excimer-forming sites occur between adjacent chromophores on the same chain; the majority of these are trans,trans meso dyads.[6] Energy migration is one dimensional, with transfer occurring mainly between adjacent chromophores. A molecular weight effect results because a migrating exciton can sample only a single chain. The length of the chain determines the number of distinct sites available for sampling.

As the PS concentration increases, excimers can form between chromophores on different chains. Also, exciton hopping from chain to chain becomes possible. When the latter occurs, the mobile exciton will no longer be limited by chain length and the molecular weight effect will vanish. Figures 1 and 2 show that this takes place above 30% PS.

It is important to note that the absence of a molecular weight effect does not imply that off-chain transfer is as efficient as down-chain transfer. At least at low PS concentrations, most hops should take place along the same chain due to the proximity of neighboring chromophores. It seems likely, however, that at high enough PS concentrations, rings on different chains will be close enough so that energy migration can be considered to be three dimensional.

1. Development of the Three-Dimensional Random Walk Model. Modeling a three-dimensional random walk exactly to fit the concentration results for toluene-cast PS/PVME blends would be very difficult. As the PS concentration increases, the number of neighbors to which transfer can take place at any step in the walk increases. From Montroll's work,[11] it is known that the stationary value of the number of distinct sites visited per step for a three-dimensional walk without emission or traps increases as the number of nearest neighbors increases. Numerical results[12] performed on random walks of similar structure show that, for a fixed number of nearest neighbors, the number of distinct sites visited per step will decrease as the walk progresses. For blends with moderately large PS concentrations, the number of distinct sites visited per step will be nearly unity, provided the walk is relatively short. Because the effect of traps and emission will be to produce walks with a small number of steps, it appears reasonable to assume that sites are not resampled during the walk. As a result, each step becomes independent and the probabilities of emission and trapping do not change at each step.

In the following derivation, the dependence of the fluorescence ratio on trap concentration and emission probability at each step will be determined for a three-dimensional random walk. The following definitions are needed in the analysis: α is defined as the probability that monomer radiative or nonradiative emission takes place before a step can be made; q is defined to be the trap concentration, which is equal to the probability that a chromophore is in an excimer-forming site.

Although the approach taken is similar to Rudemo's,[10] he assumed that the number of distinct sites visited per step was equal to its stationary value at each step. Clearly, this is not a good assumption for short walks. Furthermore, Rudemo's result does not take into account the possibility of trapping upon initial absorption of the photon, although this claim is made. Finally, whereas Rudemo's result only applies in the limit as both α and q approach zero with q/α remaining positive, the derivation in the present work will hold for all values of α and q between zero and one.

In this study, it will be assumed that if transfer to a chromophore which is in an excimer-forming site takes place, the excitation will be trapped and will be lost from the system through radiative or nonradiative decay of the excimer. Also, α should be considered to be the expected value of the fraction of times that monomer emission occurs before transfer. Since each step in the walk is independent, the probability that the excitation is trapped at the nth step is given by the product of three terms as follows.

$$P(\text{excitation is trapped at the } n\text{th step}) =$$

$$P\begin{bmatrix}\text{excitation is not}\\ \text{trapped on } n-1 \text{ steps}\end{bmatrix} \times P\begin{bmatrix}\text{excitation is}\\ \text{not emitted on}\\ n-1 \text{ steps}\end{bmatrix} \times$$

$$P\begin{bmatrix}\text{on the } n\text{th step the}\\ \text{excitation lands on}\\ \text{an excimer-forming site}\end{bmatrix} = [(1-q)(1-\alpha)]^{n-1}q \qquad (1)$$

To obtain the probability that the excitation is trapped at some point during the walk, a summation over all steps is required.

$$P(\text{excitation is trapped}) = \sum_{n=1} P(\text{trapped at } n\text{th step})$$

$$= q\sum_{n=1}^{\infty}[(1-q)(1-\alpha)]^{n-1} = \frac{q}{q+\alpha-q\alpha} \qquad (2)$$

Finally, the probability that the walk ends in monomer emission is given by

$$P(\text{monomer emission}) \equiv M =$$

$$1 - P(\text{excitation is trapped}) = \frac{\alpha - q\alpha}{q+\alpha-q\alpha} \qquad (3)$$

From the kinetic scheme used in paper 1,[8] the ratio of excimer to monomer fluorescence I_D/I_M is found to be related to the probability of eventual monomer emission M.

$$\frac{I_D}{I_M} = \frac{Q_D}{Q_M}\left[\frac{1}{M} - 1\right] \tag{4}$$

where Q_D/Q_M is the ratio of intrinsic quantum yields of excimer and monomer in the absence of interconversion between the two.

Thus

$$\frac{I_D}{I_M} = \frac{Q_D}{Q_M}\left[\frac{q}{1-q}\right]\frac{1}{\alpha} \tag{5}$$

The expected number of steps made by the migrating excitation may be determined from a similar approach, as is shown below.

Let S equal the number of steps the excitation makes before monomer emission or trapping. Here, $S = 1$ corresponds to not being trapped at the initial absorption and then being emitted before transfer or being trapped upon transfer. Since each step in the walk is independent, the probability of emision after the jth step or trapping on the $j + 1$ step is given by

$P(S = j) =$

P(not trapped j times) × P(not emitted $j - 1$ times) × [P(emitted before next step) + P(not emitted) × P(trapped)] = $(1 - q)^j(1 - \alpha)^{j-1}[\alpha + (1 - \alpha)q]$ (6)

The expected number of steps is given by

$$E[S] = \sum_{j=1}^{\infty} jP(S = j) = \frac{1 - q}{\alpha + (1 - \alpha)q} \tag{7}$$

To fit the concentration dependence of I_D/I_M, expressions for q and α must be derived in terms of the polystyrene volume fraction. A simple lattice approach will be employed in which the size of the lattice site is taken equal to the size of the PS repeat unit; the PVME segments are then broken up accordingly to fit on the same lattice. Each site with a PS repeat unit on it has a single ring. As a result of the lattice approach, the separation between rings on adjacent lattice sites will be constant, although, of course, the number of rings next to a given ring will depend on concentration. It will be assumed that transfer can only occur between rings that are nearest neighbors, that the rate of transfer between two neighbors is constant, and that the sum of the rates of transfer to each of the nearest neighbors equals the net rate of transfer from a given ring. It will also be assumed that the probability that a ring is in an excimer-forming site is the sum of the probabilities that a ring forms an excimer with each of the rings on nearest-neighbor sites.

If N is the number of nearest neighbors and ϕ is the volume fraction of PS, then $N\phi$ is the number of nearest neighbors next to a ring to which transfer may occur. This ignores the fact that polymer chains are contiguous; each PS segment, except for the chain ends, actually has at least two neighboring PS segments irrespective of the value of ϕ. If $(N - 2)\phi + 2$ were used instead of $N\phi$, however, a three-parameter model would result. It seems prudent to restrict the number of unknown parameters to a minimum, considering that for large values of ϕ where this model should apply, the dependence of I_D/I_M on ϕ shows only slight curvature. Furthermore, we note that $(N - 2)\phi + 2 \approx N\phi$ for N and ϕ reasonably large.

If k_e is defined as the rate constant for transfer to one nearest neighbor and k_M is the rate constant for monomer emission, then $N\phi k_e$ is the net transfer rate constant and

$$\alpha = \frac{k_M}{k_M + N\phi k_e} \tag{8}$$

To determine the probability that a ring is in an excimer-forming site (EFS), it is useful to separate the contributions from nearest neighbors on the same chain and rings on the other chains.

P(ring is an EFS) = P(ring is in an intramolecular EFS) + P(ring is an intermolecular EFS) (9)

i.e.

$$q = q_{intra} + q_{inter} \tag{10}$$

where

$$q_{intra} \cong 2P(\text{a given dyad is an EFS}) \tag{11}$$

It was found in paper 2[6] that at room temperature, the probability that a dyad is in the proper conformation to form an excimer is 0.025. This was determined for a chain with 45% meso dyads, a tacticity consistent with nuclear magnetic resonance results.[22] Thus, $q_{intra} = 0.05$.

The number of rings adjacent to a given ring which are not on the same chain is $(N - 2)\phi$. If the probability that two adjacent rings are in an intermolecular excimer-forming site is defined to be ζ, the concentration of intermolecular traps is

$$q_{inter} = (N - 2)\zeta\phi \tag{12}$$

The parameter ζ takes into account the geometric requirement that adjacent rings must be in a coplanar sandwich in order for excimer stabilization to take place.

Combination of the expressions derived for q and α gives

$$\frac{I_D}{I_M} = \frac{Q_D}{Q_M}\left(1 + \frac{Nk_e}{k_M}\phi\right)\left\{\frac{q_{intra} + (N - 2)\zeta\phi}{1 - [q_{intra} + (N - 2)\zeta\phi]}\right\} \tag{13}$$

In paper 2, Q_D/Q_M was found to be equal to 0.42 at room temperature. Since q_{intra} is also known, there are two unknown parameters: $N(k_e/k_M)$ and $(N - 2)\zeta$.

Equation 13 will be used to fit the concentration results for toluene-cast PS/PVME blends. As discussed above, the minimum PS concentration at which energy migration becomes three dimensional is not known. It will be assumed, somewhat arbitrarily, that this concentration corresponds to the point at which the average chromophore separation equals R_0, the Förster radius.[23] At this separation, the probability of transfer between two rings is equal to the probability of monomer emission.

The value of R_0 for polystyrene should be approximately equal to that for transfer between isopropylbenzene molecules, which has been calculated by using the overlap integral of absorption and fluorescence spectra to be 6.47 Å.[24] It would be improper to use R_0 calculated from polystyrene data because of the presence of excimers acting as traps.

If the chromophore separation is assumed to be approximately equal to (1/ring concentration)$^{1/3}$, the ring concentration corresponding to R_0 may be obtained. It is found to be 3.69×10^{-3} chromophores per Å^3. For pure polystyrene, which has a density of 1.04 g/cm^3, the chromophore concentration is 6.02×10^{-3}/Å^3. Because polystyrene and PVME have the same densities, the PS volume fraction at which the chromophore separation equals R_0 is just the ratio of these two chromophore concentrations; thus, $\phi_{PS}(R = R_0) = 0.61$.

2. Comparison with Experiment. An average of the fluorescence ratios for the two different molecular weight polystyrenes was used in the analysis. The calculation was carried out by fixing the value of $(N - 2)\zeta$ and then de-

Table I
Fitting Parameters

ϕ_{PS}	$A(\phi)^a$	$Nk_e/k_M{}^b$	$R_{exptl}{}^c$	R_{fit}
0.6	0.3089	53.58	4.30	4.18
0.7	0.3643	51.44	5.66	5.73
0.8	0.4245	51.25	7.49	7.61
0.9	0.4903	51.92	9.83	9.86
1.0	0.5625	52.24	12.58	12.54

[a] $A(\phi) = \{q_{intra} + (N-2)\zeta\phi\}/\{1 - [q_{intra} + (N-2)\zeta\phi]\}$. [b] These values of Nk_e/k_M give an exact fit. [c] These values are averages interpolated between the ratios for the two different molecular weight polystyrenes.

termining the value of Nk_e/k_M for each polystyrene volume fraction from the experimental ratio R_{exptl}. These values were then averaged and used to calculate the fit result, R_{fit}. The best fit was chosen by minimizing $\sum_\phi (R_{exptl} - R_{fit})^2$.

The best results were obtained by $(N-2)\zeta = 0.31$ and $Nk_e/k_M = 52.09$. They are shown in Table I and plotted as a solid line through the toluene-cast data in Figure 1. The fact that the values of Nk_e/k_M which give exact fits are essentially equal provides validation of the two-parameter model. In addition, it was found that if lower concentration results were included, Nk_e/k_M was no longer constant over the entire range. Thus, the applicable range of PS concentration for three-dimensional migration appears to be valid.

In order to assess the significance of the results, it is necessary to determine whether the values of the parameters used to fit the data are reasonable. It is difficult to obtain a quantitative check on the parameter $(N-2)\zeta$. Nevertheless if N, the number of nearest neighbors, is assumed to be approximately equal to 10, ζ, the probability that two adjacent rings are in an excimer configuration, is found to be of order 10^{-2}. This is consistent with the strict geometric requirements necessary for excimer formation.[6]

The value of k_e/k_M may be calculated more precisely using the theory of Förster.[23] For nonradiative energy transfer between randomly oriented chromophores

$$k_e/k_M = (R_0/R)^6 \tag{14}$$

where R is the separation between chromophores and R_0 is the Förster radius, as defined earlier. In a manner consistent with the lattice approach used in the derivation of the energy migration model, it will be assumed that the ring separation equals that found in pure polystyrene. From a simple density calculation, this leads to $R = 5.5$ Å and $k_e/k_M = 2.65$. From the best fit of the three-dimensional random walk model to the fluorescence results and assuming $N = 10$, the value of k_e/k_M is found to be about 5.2. This is reasonable agreement, considering the many simplifying assumptions employed in developing the model.

Now that the concentration dependences of α and q have been determined, the expected number of steps an exciton makes before emission or trapping can be calculated by using eq 7. If we take $(N-2)\zeta = 0.31$ and $Nk_e/k_M = 52.09$, we find that $E[S]$ changes from 2.9 to 1.7 as the polystyrene volume fraction increases from 0.6 to 1. The fact that so few hops are made is reassuring, considering that site resampling has been ignored in developing the model.

It is of interest to compare the number of steps an exciton makes at high and low polystyrene concentrations. At very low concentrations energy migration is mainly down chain; the random walk of the excitation is one-dimensional with a trap concentration $q_{intra} = 0.05$ at 300 K.[6] If emission is ignored, the expected number of distinct sites visited up to and including trapping is $(q_{intra})^{-1} = 20$. Since the number of distinct sites visited in a one-dimensional walk is of the order of the square root of the number of steps,[11] approximately 400 steps are made for the case of isolated chains. The resulting molecular weight dependence of the ratio of excimer to monomer fluorescence for low-concentration PS/PVME blends was analyzed in the previous paper.[6]

Finally, it is important to note that the nonlinear concentration dependence of the ratio of excimer to monomer fluorescence cannot be explained by a model which assumes that the only mechanism of excimer formation is direct absorption of a photon by a preformed site. The present work shows that it can be explained by including energy migration in the analysis. The simple model developed above has been found adequate and leads to fitting parameters which are reasonable.

B. Phase-Separated Blends Cast from Tetrahydrofuran. The work presented on phase-separated blends in this study is part of a larger program in which excimer fluorescence has been used to study polymer blend thermodynamics.[18-21] One of the major goals of this program is the development of excimer fluorescence as a molecular probe to determine the morphology and phase concentrations of phase-separated systems. In earlier work, the photophysics were treated in a less quantitative manner because of the lack of fluorescence data for miscible blends. It will become obvious from the following discussion why such information is required. Fortunately, both miscible and immiscible PS/PVME blends may be prepared by choosing the proper casting solvent.

In deriving an expression for the excimer to monomer fluorescence ratio of a phase-separated system, we will assume that the volume fractions of polystyrene in the rich and lean phases, ϕ_R and ϕ_L, are independent of the bulk concentration ϕ_B. From the lever rule, the volume fraction of the rich phase in the blend, V_R, is given by

$$V_R = \frac{\phi_B - \phi_L}{\phi_R - \phi_L} \tag{15}$$

The fraction of phenyl rings in the rich phase, X_R, which equals the probability that a photon is absorbed by a ring in the rich phase, is

$$X_R = \frac{\phi_R V_R}{\phi_R V_R + \phi_L(1 - V_R)} = \frac{\phi_R[\phi_B - \phi_L]}{\phi_R[\phi_B - \phi_L] + \phi_L[\phi_R - \phi_B]} \tag{16}$$

In addition, it will be assumed that there is no energy migration between phases. This is a good assumption for two reasons. The first is that polystyrene coils should be isolated in the lean phase so that the probability of off-chain transfer is small. The second is that an excitation in the rich phase should not be able to make enough hops without being trapped to escape a concentrated phase which is large enough to scatter light.

If M_R and M_L are defined to be the probabilities of eventual monomer emission from the rich and lean phases,

$$I_M = Q_M[X_R M_R + (1 - X_R)M_L] \tag{17}$$

$$I_D = Q_D[X_R(1 - M_R) + (1 - X_R)(1 - M_L)] \tag{18}$$

where Q_M and Q_D are the intrinsic quantum yields for monomer and excimer.

Thus, the ratio of excimer to monomer fluorescence is given by

$$\frac{I_D}{I_M} = \frac{Q_D}{Q_M} \frac{X_R(1 - M_R) + (1 - X_R)(1 - M_L)}{X_R M_R + (1 - X_R)M_L} \tag{19}$$

To use this expression, estimates for ϕ_R and ϕ_L must be made. Once ϕ_R and ϕ_L are fixed, M_R and M_L can be de-

termined from the fluorescence data for miscible (toluene cast) blends by using eq 4.

A good fit of the results for the THF-cast blends was obtained with $\phi_L = 0.008$ and $\phi_R = 0.98$. M_L and M_R were taken to be equal to 0.30 and 0.031, respectively, corresponding to $(I_D/I_M)_{\text{isolated PS chains}} = 0.98$ and $(I_D/I_M)_{\phi_{PS}=0.98} = 13.2$. The result of this fit is given in Figure 1, shown by the solid line through the THF-cast data. The results are insensitive to the value of Q_D/Q_M because of the empirical nature of the two-phase model. Regardless of the value of Q_D/Q_M, the same values for the rich- and lean-phase concentrations are obtained at the best fit.

Summary

For sufficiently high polystyrene concentration, a three-dimensional model for singlet energy migration has been found to explain quite well the observed dependence of I_D/I_M on concentration for PS/PVME blends. Although migrating excitons make very few hops before emission in concentrated systems, it would be difficult to explain the fluorescence results without including energy migration in the analysis. This is contrary to the claims of MacCallum.[3,4] Perhaps more important, however, is the result that excimer fluorescence can be used to study phase-separated blends quantitatively. As has been shown, a model describing energy migration it not even required to do so. The only requirement is that fluorescence data be available for a similar system for which the assumption of random mixing is valid.

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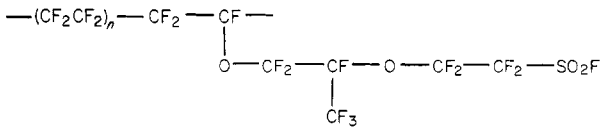
Water Relaxation in Perfluorosulfonate Ionomers

Howard W. Starkweather, Jr.,* and James J. Chang

E. I. du Pont de Nemours and Co., Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898. *Received December 23, 1981*

ABSTRACT: The sorption of water by perfluorosulfonate ionomers produces a relaxation near −100 °C in dynamic mechanical experiments. This phenomenon is also seen dielectrically and by proton NMR. When the sulfonic acid groups are neutralized with potassium or sodium, the temperature of the relaxation at low and moderate frequencies is increased and the activation energy is decreased. It is concluded that this relaxation is the glass transition of the aqueous domains in the ionomer.

Perfluorosulfonate ionomers are derived from copolymers of tetrafluoroethylene having the structure



They are characterized by their equivalent weights (EW), which are given by

$$EW = 100n + 446$$

Samples were prepared in the manner described by Gierke and co-workers.[1,2] Their crystallinity has been described in a recent paper.[3]

The sulfonyl fluoride groups can be hydrolyzed to give sulfonic acid groups or various metal sulfonates. The sulfonyl fluoride is hydrophobic, but the sulfonic acid and sulfonates absorb increasing amounts of water as the equivalent weight is decreased. Samples having equivalent weights of 1504 and 1108 in the form of $^1/_{16}$-in. sheets which had initially been exposed to a laboratory humidity were conditioned over Drierite, saturated salt solutions, or water until the weight no longer changed. The sample of EW 1504 showed no freezable water by DSC, but the sample of EW 1108 showed a small endotherm at 0 °C.

Table I
Concentration of Water in Samples Conditioned at Room Temperature

	EW 1504			EW 1108		
	K^+	Na^+	H^+	K^+	Na^+	H^+
total water, %	4.9	8.2	11.9	14.8	21.5	27.8
free water, %	nil	nil	nil	0.4	2.0	2.5
bound water, %	4.9	8.2	11.9	14.4	19.5	25.3
bound water, mol/equiv	4.1	6.9	9.9	8.9	12.0	15.6

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