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Energy Migration in the Aromatic Vinyl Polymers. 2. Miscible Blends of Polystyrene with Poly(vinyl methyl ether)

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ABSTRACT: Excimer fluorescence has been used to study the conformational properties of and energy migration in polystyrene (PS) dispersed at low concentration in miscible blends with poly(vinyl methyl ether) (PVME). Fluorescence spectra of monodisperse PS samples with molecular weights ranging from 2200 to 390 000 were taken at temperatures between 286 and 323 K and analyzed with the one-dimensional random walk model developed by Fitzgibbon.[1] The concentration of excimer-forming sites (EFS) is assumed equal to the fraction of trans,trans meso dyads obtained from rotational isomeric state calculations on chains containing 45% meso dyads. The molecular weight dependence of the ratio of excimer to monomer emission intensities is interpreted in terms of a one-dimensional random walk below 303 K. Slight deviation between the model predictions and experimental data above 303 K is consistent with a decrease in the size of the polystyrene coil caused by unfavorable thermodynamic interactions as the blend approaches the lower critical solution temperature.

Introduction

In recent years, there has been considerable interest in the photophysics of excimer formation and in energy migration in the aromatic vinyl polymers. In spite of claims to the contrary,[2] there is strong evidence for the existence of singlet energy migration, as reviewed by several authors.[3-5] It should be noted that singlet energy migration must be included in the analysis to explain the results presented in this work.

In the preceding paper of this series, referred to as paper 1, energy migration in an isolated polymer chain was treated as a one-dimensional random walk of the electronic excitation between adjacent pendant chromophores.[1] At each step in the walk, the excitation can be lost radiatively or nonradiatively from an isolated excited chromophore or "monomer". Alternately, the excitation can be trapped at an excimer-forming site (EFS) composed of two adjacent chromophores, leading to radiative or nonradiative emission from the excimer. This approach has been proposed to explain the molecular weight dependence of the ratio of excimer to monomer emission intensities for isolated extended chains.[1]

The purpose of this work is to test the one-dimensional energy migration model quantitatively using a well-characterized system and in so doing to demonstrate how the technique of excimer fluorescence can be used to study conformational properties of polymers. Several criteria must be satisfied, however, before the model may be applied. First, the fluorescent guest polymer must be dispersed at sufficiently high dilution to eliminate both intermolecular excimer sites formed between chromophores on different chains and intermolecular energy migration. Second, the solvent or host matrix must be sufficiently good thermodynamically to minimize intramolecular interaction between aromatic rings on remote repeat units of the guest. Finally, the rate of segmental motion must be much slower than the rate of energy migration, so that excimer-forming sites are immobile and rotational sampling may be ignored. In solution studies such as those analyzed in the preceding paper it is possible that this final requirement is not met at high temperatures.

All of the necessary specifications are met, however, by the physical blend of polystyrene with poly(vinyl methyl ether). Film casting from toluene has been shown by a variety of experimental techniques[6-10] to lead to apparently miscible systems; thus, low-concentration blends should contain isolated polystyrene chains. In addition, the low glass transition temperature of PVME (245 K) ensures that all low-concentration blends studied will be in the rubbery state. As a result, the conformational population of the polystyrene chains may be assumed to be in equilibrium. Since conformational energy maps exist for polystyrene[11-13] rotational isomeric state calculations of the equilibrium dyad population may be made. Finally, the rotational sampling rate is expected to be inhibited strongly relative to other studies[14-16] in which polystyrene has been examined in solution.

Experimental Section

Polystyrene samples of molecular weights 2200, 4000, 9000, 17 500, 35 000, 100 000, 233 000, and 390 000 were obtained from Pressure Chemical Co.; they have polydispersities less than or equal to 1.06. 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 its intrinsic viscosity in benzene at 303 K. Because of its low glass transition temperature, a special purification technique had to be developed for the 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, all at a concentration of 5% by weight of PS, were prepared by casting from toluene solution onto sapphire disks at room temperature. Preliminary concentration studies show that at this concentration, the PS chains are isolated. The films were then dried under vacuum at 323 K for at least 4 days to ensure removal of the casting solvent. No evidence of residual solvent was found from the fluorescence spectra of neat

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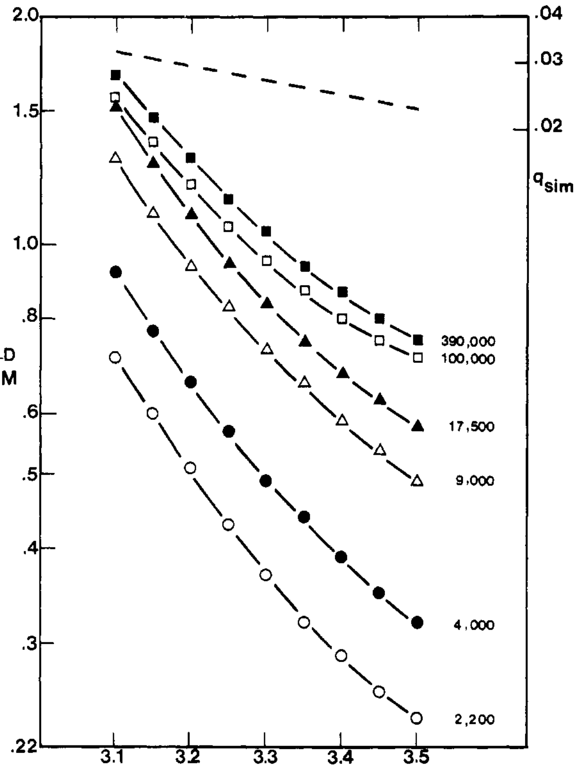

Figure 1. Temperature dependence of the ratio of excimer to monomer fluorescence intensities and the tt meso dyad population. Smooth curves are drawn through the experimental fluorescence data; the notation by each curve indicates the molecular weight of the monodisperse polystyrene. The dashed line illustrates the results of a Monte Carlo simulation to determine the excimer-forming site trap concentration.

PVME films prepared under identical conditions.

Fluorescence spectra were taken under a nitrogen atmosphere using a spectrofluorimeter that has been described earlier.[17] The sample was excited at 260 nm in a front-face arrangement to minimize self-absorption. Simple fluorescence intensities were measured at 280 nm (monomer) and 332 nm (excimer), where there is no overlap of excimer and monomer bands.

Before spectra were taken, the films were annealed for 10 min at the desired temperature. Temperature control was within ±0.25 K for all measurements. The ratio showed no time dependence after 10 min over the temperature range from 286 to 323 K. At temperatures less than 286 K, the ratio of excimer to monomer fluorescence intensities (I_D/I_M) did exhibit a time dependence, indicating that the PS chains were not in conformational equilibrium. The upper temperature limit was chosen low enough to preclude thermal deactivation of the excimer, which would complicate the analysis. Previous quenching studies[14,15,18] and time-resolved fluorescence spectroscopy[19] of PS in solution and fluorescence spectroscopy of neat PS films[20] show that thermal deactivation of excimer to excited monomer is unimportant, at least at room temperature.

Results

1. Fluorescence Data. The polystyrene fluorescence data have been plotted in two different forms in Figures 1 and 2. In these plots, smooth curves have been drawn through the data. Figure 1 shows that I_D/I_M increases with increasing temperature for any given molecular weight. Contrary to earlier results for polystyrene in fluid solutions,[14,15] this behavior is not perfectly Arrhenius. The magnitude of the change in I_D/I_M with temperature increases as the molecular weight of the polystyrene is lowered.

In Figure 2, I_D/I_M is plotted as a function of polystyrene molecular weight for different film temperatures. In all cases, the ratio increases rapidly with chain length at low molecular weights but much more slowly at high molecular weights. Similar molecular weight dependence has been observed for P2VN in solution[21] and solid blends[22] and for PS in solution.[15,16] The solution results for P2VN were analyzed in paper 1.

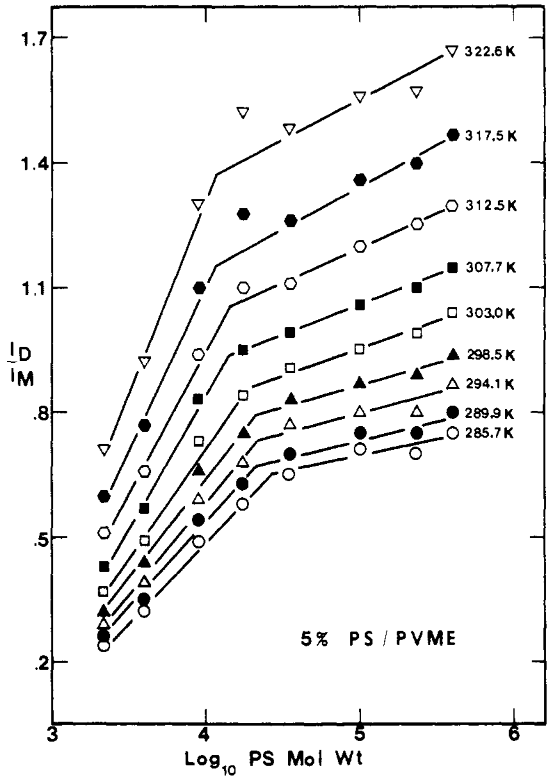

Figure 2. Molecular weight dependence of the ratio of excimer to monomer fluorescence intensities. This is an alternative representation of the same data as Figure 1.

A significant observation is the persistence of the molecular weight dependence at high molecular weight. This dependence is measurable, but small, for temperatures less than about 303 K. At higher temperatures, however, the effect becomes more pronounced. Similar behavior has been found for PS in thermodynamically poor solvents.[16]

2. Determination of Excimer-Forming Site Concentration in Polystyrene. As explained in the next section, the EFS concentration is required in order to fit the fluorescence data using the random walk model. Several studies of the conformational statistics of polystyrene and its model compounds have been made.[11-13] Ignoring solvent effects, Gorin and Monnerie[11] determined the conformational energies for meso and racemic 2,4-diphenylpentanes. They found that conformations of the racemic form which have the ring–ring overlap required for excimer formation are at extremely high energies. In addition, their calculations showed that the lowest energy state of the meso stereoisomer is the tt conformation, which has the proper geometry for excimer formation.

In a study of the conformational statistics of polystyrene, Yoon, Sundararajan, and Flory employed a two-state rotational scheme[12] where $\bar{g}$ states were assumed to be insignificant due to steric interactions. In this approach, excimer formation can result only from tt meso dyads. Yoon et al. drew the same conclusions as Gorin and Monnerie about the meso dyad energies in the absence of solvent effects. However, when solvent effects were taken into account, the tt conformation was no longer lowest in energy.

Finally, in a recent study by Stegen and Boyd,[13] the analysis was extended to three rotational states. At 298

K, the EFS concentration of the meso form of 2,4-diphenylpentane was calculated to be 0.045 while that of the racemic for was found to be 0.0026.

In summary, conformational studies of polystyrene and its model compounds show that racemic dyads can be ignored when the EFS concentration is calculated for atactic chains with a significant meso content. Specifically, only the concentration of tt meso dyads need be considered.

It is also of interest to examine experimental data on excimer fluorescence in stereoregular model compounds. The first work in this area was done by Longworth and Bovey,[23] who examined meso and racemic 2,4-diphenylpentanes in 3-methylpentane at 298 and 77 K. More recently, Bokobza, Jasse, and Monnerie[24] studied excimer formation in several oligomers: 2,4-diphenylpentane, 2,4,6-triphenylheptane, and 2,4,6,8-tetraphenylnonane. Both meso and racemic compounds were examined at 298 K in dichloroethane.

In order to compare the two sets of results, we have estimated $I_D/I_M \equiv R$ for each compound from the envelope intensities at 332 nm (excimer) and 280 nm (monomer). There is good agreement in the data for 2,4-diphenylpentane. Longworth's results[23] give $R_{\text{meso}}/R_{\text{racemic}} = 5.9$ while those from Monnerie give $R_{\text{meso}}/R_{\text{racemic}} = 5.6$. We note, however, that there is some additional structure in the fluorescence spectrum of Longworth's compound which was not found in the later study. When calculated in the same manner, $R_{\text{meso}}/R_{\text{racemic}}$ values for the triphenyl and tetraphenyl compounds of Monnerie are found to be 8.6 and 9.8, respectively.

Although the solution studies support the claim that the contribution of EFS from racemic dyads is small, there are difficulties in applying these results to an analysis of the site population of polystyrene dispersed in a solid blend. In fluid solution, excimer formation is a dynamic process involving bond rotation. This is not the case for PS/PVME blends. As a result, it seems appropriate to emphasize the conformational calculations rather than the fluorescence observations in support of the assumptions made in this work.

In order to determine the concentration of tt meso dyads in an atactic PS chain, the analysis developed by Flory[25] has been followed. In this treatment, the probability that dyad r is in state $\beta\gamma$ on a chain made up of x repeat units is given by

$$P_{\beta\gamma;r} = Z^{-1}\mathbf{J}^*\left(\prod_{n=1}^{r-1}\mathbf{U}_n^{(2)}\right)(\mathbf{U}'_r\mathbf{U}''_{\beta\gamma r})\left(\prod_{n=r+1}^{x-1}\mathbf{U}_n^{(2)}\right)\mathbf{J} \qquad (1)$$

in which Z is the partition function

$$Z = \mathbf{J}^*\left(\prod_{r=1}^{x-1}\mathbf{U}_r^{(2)}\right)\mathbf{J} \qquad (2)$$

and the matrices are defined as

$$\mathbf{J}^* = [1 \quad 0] \qquad \mathbf{J} = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \qquad \mathbf{U}^{(2)} = \mathbf{U}'\mathbf{U}''$$

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \qquad \mathbf{U}''_{\text{meso}} = \begin{bmatrix} w'' & 1/n \\ 1/n & w/n^2 \end{bmatrix}$$

$$\mathbf{U}''_{\text{racemic}} = \begin{bmatrix} 1 & w'/n \\ w'/n & 1/n^2 \end{bmatrix}$$

The matrix $\mathbf{U}''_{\beta\gamma}$ is formed from the matrix $\mathbf{U}''$ by setting all elements except for the statistical weight for state $\beta\gamma$ equal to zero.

The statistical weight matrix $\mathbf{U}'$ takes into account second-order interactions for bonds surrounding a CHR group whereas $\mathbf{U}''$ takes into account first- and second-order interactions related to the state of the two bonds surrounding a CH_2 skeletal group. The values of the statistical weights have been reported[12] as

$$w = w' = 1.3 \exp(-1000/T)$$

$$w'' = 1.8 \exp(-1100/T)$$

$$n = 0.8 \exp(200/T)$$

Table I
Results Obtained from the Random Walk Model and from Monte Carlo Simulations

T, K	$1/T \times 10^3$, K^{-1}	q_{sim} [a]	Q_D/Q_M [b]	α	$\Sigma(R_{\text{exptl}} - R_{\text{fit}})^2$
285.7	3.50	0.0227	0.36	6.01×10^{-4}	8.38×10^{-3}
289.9	3.45	0.0237	0.38	6.47×10^{-4}	7.46×10^{-3}
294.1	3.40	0.0248	0.42	7.14×10^{-4}	9.66×10^{-3}
298.5	3.35	0.0259	0.43	7.65×10^{-4}	8.28×10^{-3}
303.0	3.30	0.0270	0.49	8.31×10^{-4}	1.21×10^{-2}
307.7	3.25	0.0282	0.53	9.12×10^{-4}	1.39×10^{-2}
312.5	3.20	0.0294	0.63	1.06×10^{-3}	2.07×10^{-2}
317.5	3.15	0.0308	0.74	1.21×10^{-3}	2.40×10^{-2}
322.6	3.10	0.0321	0.87	1.36×10^{-3}	2.55×10^{-2}

[a] Results are from Monte Carlo simulations on infinite molecular weight chains. [b] Q_D/Q_M was chosen so that at the best fit of the data, the trap concentration equaled that from conformational calculations.

In a purely isotactic polystyrene chain of infinite molecular weight, the tt meso dyad population may be calculated analytically;[25] it has been found to be 13.4% at 300 K. In atactic chains, however, the trap concentration must be obtained by using a Monte Carlo simulation. This is because the average conformation of a specific dyad is subject to wide variation, depending on the stereochemical configuration of sequences of dyads adjoining the one in question.[25]

In order to carry out the simulation, the meso dyad content was fixed at 45%, which is consistent with the results from nuclear magnetic resonance.[26] An ensemble of chains of the desired molecular weight and tacticity was then generated randomly. For each chain in the ensemble, the partition function and the probability that each dyad was in a tt meso state were calculated. Averaging of the dyad population over the ensemble allowed the trap concentration to be determined. In all cases, the ensemble was large enough to obtain a stationary distribution. The size of the ensemble necessary to obtain reproducibility in trap concentration to three significant figures decreased from 5000 to less than 3000 chains as the molecular weight increased from 2200 to 17 500. The computer code for the simulation was verified by reproducing the trap concentration for the isotactic chain of high molecular weight.

The results of the simulation are presented as q_{sim} in Table I and as the dashed line in Figure 1. For chains with 45% meso dyads, the trap concentration showed little dependence on molecular weight over the temperature range studied. For example, at 303 K, q_{sim} varied from 0.0261 for a molecular weight of 2200 to 0.0270 at the stationary distribution corresponding to molecular weights greater than or equal to 17 500. This small effect was ignored in the analysis and all reported values of q_{sim} refer to the stationary distribution. The trap concentration was strongly temperature dependent, however, as shown by the Arrhenius-like behavior of the dashed line in Figure 1. The effective EFS energy, i.e., the equilibrium separation between the potential energy minima for the preferred and the tt meso conformations, is 1.7 kcal/mol.

The Monte Carlo simulation shows that the presence of racemic dyads lowers the probability that a meso dyad is in the tt conformation. For example, at 300 K a simulated atactic chain with 45% meso dyads has a tt meso concentration of about 2.6%. On the other hand, simple multiplication of the fraction of meso dyads by the tt dyad population for an isotactic chain yields a value of about 6.0%. Clearly, Monte Carlo simulations are required in order to deal quantitatively with the conformational statistics of an atactic chain.

3. Application of the One-Dimensional Random Walk Model. In paper 1 it was shown that, in the absence of quenchers, the ratio of excimer to monomer fluorescence intensities is given by

$$\frac{I_D}{I_M} = \frac{Q_D}{Q_M}\left[\frac{1}{M(\alpha,q,L)} - 1\right] \tag{3}$$

in which Q_D/Q_M is the ratio of intrinsic quantum yields for excimer and monomer fluorescence, $M(\alpha,q,L)$ is the overall probability that an absorbed photon leads to monomer emission by both radiative and nonradiative means, α is the probability of monomer emission both radiatively and nonradiatively at any step in the random walk, q is the trap or EFS dyad fraction, and L is the chain length.

Four assumptions were made in applying the one-dimensional random walk model to the fluorescence data. The first, that the trap concentration is independent of molecular weight, has already been justified in the previous section on conformational statistics.

The second assumption is that α, which is equal to one minus the probability of transfer at each step, is also independent of molecular weight. Because different conformations result in different orientations and distances between adjacent aromatic rings, α is, in fact, not constant at each step in the walk and should be viewed as an averaged or global probability. Nevertheless, since the concentrations of the various conformations do not depend on molecular weight, α should be independent of chain length. An analysis of the temperature dependence of α would be exceedingly complex and has not been attempted.

Third, thermal deactivation of the excimer to excited monomer has been ignored. It is known that it does not occur below room temperature,[14,15,18-20] and there is no evidence in the present data to suggest that it occurs at the higher temperatures studied in this work.

Fourth, the existence of quenchers was ignored to simplify the analysis. Care was taken in moving all films from a vacuum oven to a nitrogen atmosphere rapidly to minimize the exposure to oxygen.

Q_D/Q_M has been regarded as a parameter in this study, although in principle it can be measured. As shown in paper 1, in the absence of thermal deactivation of the excimer

$$\frac{Q_D}{Q_M} = \frac{\phi_D}{Q_0 - \phi_M} \tag{4}$$

where ϕ_D and ϕ_M are the quantum yields of excimer and monomer fluorescence of polystyrene and Q_0 is the quantum yield of a suitable single-ring compound placed in the same PVME host matrix at the same concentration of chromophores. Unfortunately, the preparation of a film in which a low molecular weight compound is dispersed uniformly at a known concentration is difficult, even for compounds of relatively low volatility. In addition, the measurement of quantum yields instead of intensity or quantum yield ratios would require films with extremely uniform thicknesses, which are difficult to obtain.

Thus, for a given temperature, the model has three parameters: α, q, and Q_D/Q_M. It was found, however, that the combination of the three parameters which gave the best fit of the fluorescence data at a given temperature was not unique. As a result, the data were analyzed by varying Q_D/Q_M and α so that at the best fit, the trap concentration obtained from the experimental results matched that from the conformational calculations described in the previous section. The approach followed is illustrated in flow sheet form in Figure 3. The results of the analysis, together with the trap concentration from conformation calculations, are given in Table I. In Figure 4, data at three temperatures are replotted together with smooth curves showing the results of the fit.

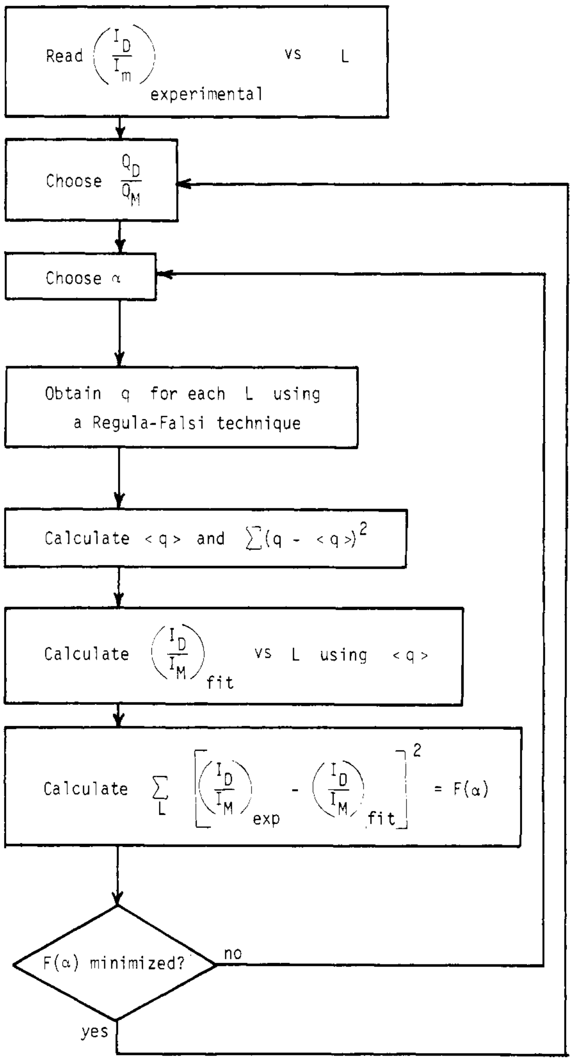

Figure 3. Flow diagram illustrating the method of fitting the experimental data of I_D/I_M as a function of molecular weight with the one-dimensional random walk model.

From the value of the residual given in the final column in Table I, it is apparent that above 303 K, the one-dimensional random walk model does not fit the data as well as below 303 K. This can also be seen in Figure 4, which demonstrates that the model does not predict the observed persistence of the molecular weight dependence of the ratio at the highest molecular weights.

The results of the fit also show that Q_D/Q_M is of order 10^{-1} and increases with increasing temperature. The reported values of Q_D/Q_M include an instrument response factor and a factor which converts band intensity ratios to area ratios. To obtain a true value of Q_D/Q_M, it should be multiplied by a correction factor between 1 and 2. This was determined by a comparison of the ratio obtained using uncorrected intensity measurements and that obtained using band areas of spectra corrected for instrument

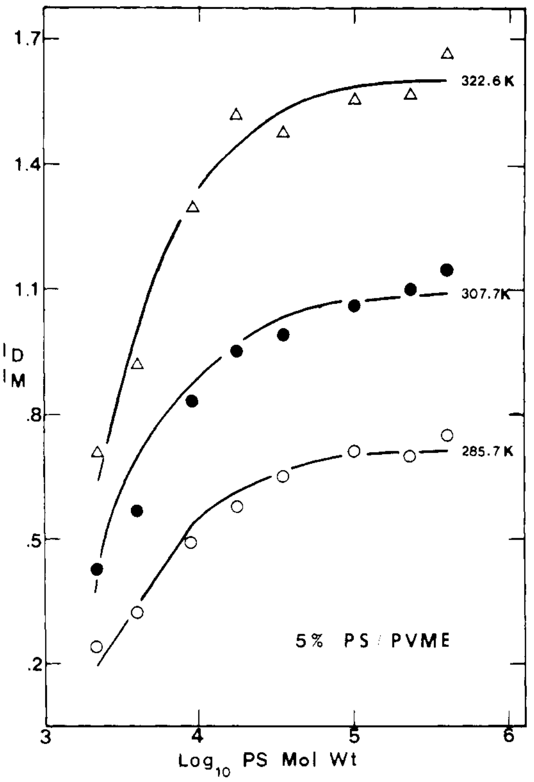

Figure 4. Comparison of experimental fluoresence results with the best fit from the one-dimensional random walk model (solid curve) for several temperatures.

response. The uncertainty in the correction factor is a result of the difficulty in separating the excimer and monomer bands in the region of overlap. Once an arbitrary method is chosen, however, the correction factor is independent of temperature and the magnitude of the ratio.

Although, as previously discussed, it is difficult to measure Q_D/Q_M for polystyrene dispersed in PVME, it has been determined for polystyrene and polystyrene model compounds in fluid solution. Thus, an order of magnitude check of the values of Q_D/Q_M obtained from the fit of the fluorescence data with the random walk model can be made.

Q_D/Q_M has been measured for the case of intermolecular as well as intramolecular excimers. For toluene in methylcyclohexane, Q_D/Q_M was found to be equal to 0.175 at 298 K and 0.104 at 195 *K*.[27] In another study of toluene in hexane at 298 K, a value of 0.35 was obtained.[28] An increase in Q_D/Q_M with increasing temperature was also oberved for benzene in cyclohexane;[29] here a value of 0.38 at 298 K was reported.

For intramolecular excimer-forming compounds, Q_D/Q_M can be obtained by using eq 4 from literature values of quantum yields of excimer and monomer fluorescence if the quantum yield of a suitable single-ring compound such as isopropylbenzene has been measured in the same solvent. Data for isopropylbenzene exist for cyclohexane,[30] dioxane, methylene chloride, and dichloroethane[31] solutions. From fluorescence results of polystyrene oligomers in methylene chloride at 298 K, Q_D/Q_M ranged from 0.26 for the meso form of 2,4-diphenylpentane to 0.42 for the syndio form of 2,4,6,8-tetraphenylnonane.[24] For atactic polystyrene at 298 K, Q_D/Q_M ranged from 0.05 in cyclohexane[32] to 0.283 in methylene chloride.[31] Q_D/Q_M has been found to depend on tacticity for both oligomers[24] and the polymers.[32]

To summarize, values of Q_D/Q_M at 298 K ranging from 0.05 to 0.42 have been observed. It appears that Q_D/Q_M depends not only on environment and whether excimers are formed intramolecularly or intermolecularly but also on tacticity for the intramolecular case. Despite the uncertainty in the correction factor in the present work, the values of Q_D/Q_M obtained from the fits of the fluorescence data with the random walk model are certainly reasonable.

The increase in Q_D/Q_M with increasing temperature observed in this work has also been observed for the case of intermolecular excimers.[27,29] The magnitude of Q_D/Q_M found above 303 K may be artificially large, however, since the one-dimensional random walk model does not fit the high-temperature data so well. Finally, it appears that the neglect of thermal deactivation of the excimer at high temperatures is a good assumption. Thermal deactivation of the excimer would have resulted in a decrease with increasing temperature of Q_D/Q_M obtained from the fit since the trap concentration was matched with the results of conformational calculations. The opposite trend was found.

Discussion

Before we proceed with the discussion of the one-dimensional random walk model and the implications of its use as a tool for the study of polymer conformational properties, it is informative to assess the importance of singlet energy migration in the system under study. This can be accomplished by making an order of magnitude calculation of the I_D/I_M ratio in the absence of energy migration.

Since rotational sampling does not occur in a solid solution, the probability that an absorbed photon leads to monomer emission in the absence of energy migration is equal to $1 - 2q$, where $2q$ is the fraction of chromophores that are in excimer-forming sites. Using this and eq 3 leads to

$$\frac{I_D}{I_M} = \frac{Q_D}{Q_M}\left[\frac{2q}{1 - 2q}\right] \qquad (5)$$

Noting from the conformational calculations that q is approximately 10^{-2} and from studies on polystyrene and its model compounds[27-32] that Q_D/Q_M is of order 10^{-1}, I_D/I_M would be estimated to be of order 10^{-3}. Clearly, since the experimental I_D/I_M is of order unity, energy migration must be included in the analysis.

Although several experimental studies and attempts at analysis have been performed, the effect of chain length on the ratio of excimer to monomer fluorescence has not as yet been explained satisfactorily. For example, it has been postulated that the molecular weight effect in solution derives from the greater effectiveness of rotational motion for bonds near the ends of a chain.[15,21] This explanation cannot be used for the PS/PVME blend because of its high viscosity.

Another explanation that has been offered for polystyrene in solution is that the trap concentration increases rapidly with molecular weight.[15] In that study, however, a model which ignores both energy migration and the temperature dependence of rotational sampling was used. Conformational calculations presented in this work show that the trap concentration depends little on molecular weight.

A major problem with previous analyses has been a neglect of the random walk nature of the energy migration process. The interested reader unfamiliar with the theory of random walks may wish to refer to Barber's review of the literature.[33] A random walk analysis was employed previously for the blend of poly(2-vinylnaphthalene) with polystyrene.[22] Unfortunately, the authors first used a kinetic scheme which implicitly ignores the one-dimensional character of the walk and then used a three-dimensional random walk model to determine the number of steps an exciton makes during its lifetime. As shown in paper 1, this type of modeling is incorrect for truly isolated and extended chains in which migration occurs mainly between adjacent chromophores.

This work demonstrates that at temperatures below 303 K, the molecular weight dependence of the fluorescence ratio for the PS/PVME may be quantitatively explained in terms of a one-dimensional random walk of the excitation. The walk is expected to be one-dimensional when the chains are isolated and relatively extended and the trap concentration is small. Because of the small probability of emission at each step, sites are sampled over and over. For short chains, there is a smaller probability of finding a trap due to the low trap concentration; indeed, for very short chains there may be no EFS traps at all. An increase in the molecular weight will yield more distinct sites available for sampling so that the probability of finding a trap will increase.

The ratio levels off at higher molecular weights for two reasons. The first is that the lifetime of the excitation is finite so that the length of the chain which can be sampled is limited. This effect is enhanced by the "inefficiency" of a one-dimensional walk resulting from the resampling of sites. More specifically, the number of distinct sites visited in n steps for a one-dimensional walk without emission and traps is proportional to $n^{1/2}$.[33] The second reason is that the trap concentration is finite. This has the effect of dividing long chains into shorter segments, thus making longer chains appear photophysically similar.

These proposals also explain the effect of temperature on the ratio below 303 K. Increasing the temperature will increase the trap concentration because the tt conformation is higher in energy than other meso dyads. This will, of course, lead to an increase in the ratio. Longer chains will be affected less because of the larger number of sites available for sampling. Thus, ratios for shorter chains should show a stronger temperature dependence, as has been observed here.

The final point of interest regards the observed non-Arrhenius temperature dependence. This is caused in part by the increase in Q_D/Q_M with temperature. It is interesting to note, however, that such behavior could also occur even if Q_D/Q_M were constant. This may be understood by reference to Barber's[33] discussion of a one-dimensional walk without emission. Barber finds the probability that the exciton walker will return to the origin before being trapped to be given by

$$P_{\text{return}} = 1 + \frac{2q}{1 - 2q} \ln 2q \qquad (6)$$

where $2q$ is the trap concentration. Correspondingly, the probability that the walker is trapped before returning to the origin is

$$P_{\text{trap}} = 1 - P_{\text{return}} = -\frac{2q}{1 - 2q} \ln 2q \qquad (7)$$

which increases faster than the trap concentration. Thus, when energy migration is present, an increase in the trap concentration will lead to less resampling and a more efficient walk. This will result in a more rapid increase in I_D/I_M with temperature than would be expected in the absence of energy migration.

Although the model works well at low temperatures, fluorescence data taken at and above 303 K are not fit as well. The model cannot fit data in which the molecular weight effect persists in the high molecular weight range. It appears that at the higher temperatures studied, the random walk of the excitation is no longer perfectly one-dimensional over all or part of the PS molecular weight range.

There are two possible explanations of why the dimensionality of the random walk might change in the PS/PVME blends. The first is based on the observation in a number of studies[7-10,34] of the existence of a lower critical solution temperature. Phase separation would lead to intermolecular transfer of the excitation between aggregated polystyrene chains, imparting a three-dimensional character to the walk. This is unlikely to be the reason for the particular combination of temperatures, molecular weights, and concentration used in this study, however. Previous workers have shown that phase separation in the PS/PVME blend should not occur for any of the PS molecular weights used until above 373 K.

A second possibility is that there is a decrease in the PS coil dimensions with increasing temperature as a result of adverse thermodynamic interactions with the PVME host matrix. This would cause energy migration across loops in the chain to occur, also resulting in a more efficient walk due to the increased dimensionality. Although there is no independent evidence for this phenomenon in the PS/PVME blend, a comparison of the results of this study with those from other investigations is most enlightening. For example, a study in fluid solution of energy transfer from naphthalene groups in poly(1-naphthyl methacrylate) to vinylanthracene traps located at chain ends showed that the efficiency of transfer increased in solvents which reduce the coil dimensions.[35] Furthermore, in a study of polystyrene fluorescence in various solvents, it was found that changing the solvent quality changed both the dependence of I_D/I_M on molecular weight and the magnitude of the ratio.[16] In poor solvents, the molecular weight effect persisted to higher molecular weights after the initial rapid increase, and the ratios were larger. An explanation involving formation of excimers between nonadjacent chromophores was examined and rejected.

It is well-known that decreasing the solvent quality decreases the coil dimension of a polymer. While this may affect the conformational populations slightly, a more important factor is that it will allow more facile transfer across loops. The resulting increase in the dimensionality of the walk makes energy migration more efficient; the number of distinct sites visited during the walk increases. For example, for a three-dimensional walk on a periodic lattice, the number of distinct sites visited in n steps is proportional to n. Of course, this increase in migration efficiency will cause an increase in the ratio. It also will allow the excitation to sample longer chain segments before emission takes place, resulting in a persistence of the molecular weight effect.

It is interesting to note that in solution,[16] the effect of temperature on the ratio for a given solvent is the opposite of what was found for the PS/PVME blend. In solution, decreasing the temperature caused a persistence of the molecular weight effect. This is consistent with the fact that decreasing the temperature of a polymer–solvent system generally leads to a lower miscibility and a decreased coil dimension of the polymer, while for polymer blends, the opposite is usually expected. This behavior is the rule rather than the exception, as shown by the experimental evidence that for the case of no specific interactions polymer–solvent systems exhibit an upper critical solution temperature while polymer blends exhibit 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)

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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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