

# Excimer fluorescence as a molecular probe of polymer blend miscibility: 8. Polymeric and glassy solvent host matrices

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The effects of solubility parameter differences between the guest polymer and the host matrix and of guest molecular weight on the thermodynamic miscibility and chain configuration of poly(2-vinylnaphthalene) (P2VN) dispersed in polymeric or glassy solvent hosts are investigated using excimer fluorescence. For P2VN blends with a series of poly(alkyl methacrylates) in which the difference in the guest and host solubility parameters is minimized, the small increase in the excimer to monomer fluorescence ratio,  $I_D/I_M$ , with increasing P2VN molecular weight can be rationalized by a one-dimensional energy migration model proposed by Fitzgibbon and Frank. The results indicate the possibility of small-scale phase separation or local coil contraction for P2VN with molecular weight greater than 21000. As the thermodynamic interaction between the guest and polymeric host is altered towards immiscibility,  $I_D/I_M$  can be related to the extent of intermolecular aggregation in the blend. To study the efficiency of intramolecular energy migration independent of intermolecular association and free of casting solvent effects, we chose a host system consisting of a series of monomeric glassy solvents. The rate of energy transfer is investigated by transient fluorescence and treated by a one-dimensional model developed by Fredrickson and Frank. The results are in excellent agreement with independently measured photostationary-state fluorescence ratios.

(Keywords: excimer fluorescence; molecular probe; blends; miscibility)

## INTRODUCTION

This is part of a series of papers<sup>1-14</sup> in which excimer fluorescence is employed as a molecular probe for the analysis of the morphology of blends formed by dispersing an aromatic vinyl polymer as a guest in solid polymer host matrices. Previous work has demonstrated that excimer fluorescence has the required sensitivity to detect small-scale phase separation and low-concentration immiscibility at an earlier stage than is possible by measurements of optical clarity or differential scanning calorimetry<sup>4,6-7</sup>. A convenient experimental quantity is the ratio of excimer to monomer emission intensities,  $I_D/I_M$ , obtained under photostationary-state excitation. An excimer is a dimeric complex formed between two adjacent aromatic chromophores sharing the same quantum of excitation energy through  $\pi$ - $\pi$  electronic interactions. The interpretation of changes in  $I_D/I_M$  occurring as a result of changes in polymer host and guest molecular weights, thermodynamic compatibility and concentration is not a trivial task. It is even more difficult to interpret the absolute value of  $I_D/I_M$  in terms of molecular parameters such as the chain configuration or the local segment density<sup>1,2,14</sup>.

The difficulty lies in the fact that the photophysics of the aromatic vinyl polymers is quite complex. In general, each pendant aromatic chromophore can absorb unpolarized light and the excitation energy can migrate among the ensemble of chromophores before eventually undergoing non-radiative or radiative decay<sup>8-9,15</sup>. As an

alternative to monomer deactivation, the migrating exciton can be trapped by either intramolecular or intermolecular excimer-forming sites (EFS). An understanding of the coupled interaction between the number and types of EFS traps and the nature of the electronic excitation transport (EET) process is essential for a description of the chain structure and the blend morphology.

In earlier attempts at relating the photophysical observables to the morphology of polymer blends, we focused on several variables important to polymer-polymer miscibility: concentration of the guest polymer in the host matrix<sup>2,3</sup>, molecular weights of the guest and host polymers<sup>4,6-7</sup>, and the casting temperature<sup>1,5</sup>. We showed that the simple Flory-Huggins mixing theory could be used to predict the points of immiscibility arising from increases in guest or host molecular weight in blends of poly(2-vinyl naphthalene) (P2VN) with both polystyrene (PS) and poly(methyl methacrylate) (PMMA)<sup>4,10</sup>. For components having only dispersive interactions, i.e. no specific interactions such as hydrogen bonding or polar attraction, regular solution theory has been shown to yield a reasonable estimate of the binary interaction parameter of the blend<sup>16</sup>.

In the first paper of this series, Frank and Gashgari applied excimer fluorescence to investigate the miscibility of blends formed from dispersion of 0.2 wt % P2VN in a homologous series of poly(alkyl methacrylates)<sup>1</sup>. Maximum dispersion of the P2VN guest in the host matrix was expected when the two polymers have the same solubility parameter. The poly(alkyl methacrylate)

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host matrices selected provide for such molecular dispersion since the range of their solubility parameter brackets that of P2VN. Indeed  $I_D/I_M$  passed through a minimum when the guest and host solubility parameters were equal. A value of  $8.85 \text{ cal}^{1/2} \text{ cm}^{-3/2}$  was estimated for the solubility parameter,  $\delta$ , of P2VN with viscosity average molecular weight,  $M_v$ , of 71 000 as a guest in the poly(alkyl methacrylate) host matrix series. Similar results were found for poly(acenaphthalene) and poly(4-vinylbiphenyl) dispersed in the same homologous host matrix series<sup>2,3</sup>.

Analogous behaviour was subsequently observed for aromatic vinyl polymers in solvent series and solvent mixtures. Soutar<sup>17</sup> measured  $I_D/I_M$  in poly(1-vinylnaphthalene) and poly(1-vinylnaphthalene-co-methyl methacrylate) in mixed solvent systems of toluene/methanol and toluene/cyclohexane. A minimum in  $I_D/I_M$  was observed when the solubility parameter of the solvent matched that of the polymer guest. Li *et al.*<sup>18</sup> estimated the  $\delta$  of PS in a variety of monomeric solvents by tagging the PS chain with pyrene groups at regularly spaced intervals, and monitoring the pyrene excimer to monomer fluorescence ratio. Their results yielded a value of 9.1 for  $\delta_{PS}$ , which agrees quite well with published data.

The present paper focuses on the enthalpic interactions of aromatic vinyl polymers in polymeric and glassy solvent host matrices. Of course it is the free energy of the mixing process that will govern whether a one- or two-phase system will be formed at equilibrium. However, in blends of high molecular weight polymers, the entropic contribution to the free energy of mixing is generally overshadowed by the enthalpic contribution<sup>6,7</sup>.

Our first objective was to extend the early photostationary-state fluorescence work by Frank and Gashgari<sup>1-3</sup> for P2VN blended with a homologous series of polymer hosts. We approach this along two lines: effects of P2VN guest molecular weight on  $I_D/I_M$  relative to the difference in solubility parameters between guest and host, and incorporation of pyrene labels as low energy traps of fixed composition. The photostationary results are interpreted in terms of a one-dimensional energy migration model<sup>11</sup> for isolated P2VN coils and in terms of microphase separation in thermodynamically poor host matrices.

Our second objective was to assess the applicability of a one-dimensional EET model developed by Fredrickson and Frank<sup>19</sup> to characterize isolated P2VN coils in a series of monomeric glassy solvents at 113 K. For the first time in this type of study, transient fluorescence was used to investigate the efficiency of EET and trapping in the guest polymer. A host matrix series consisting of monomeric solvents at low temperature provides a true binary system. Furthermore, at the low temperature of 113 K, bulk polymer diffusion should be eliminated and segmental rotation should be drastically reduced. Thus, the P2VN coil will be frozen in a configuration determined by the thermodynamic compatibility of the solvent-host system. The one-dimensional EET model of Fredrickson and Frank addresses directly the rate of energy migration among chromophores with an average distance of separation. An increase in the efficiency of EET reflects a change in the average chromophore separation distance, which can be correlated with changes in thermodynamic compatibility.

## EXPERIMENTAL

**Materials.** One of the P2VN samples with  $M_v$  equal to 71 000 was prepared by bulk thermal polymerization, as described previously<sup>4,6-7</sup>. Examination by a Waters Associates gel permeation chromatograph system equipped with six  $\mu$ -Styragel columns (80-800A) and a Pye Unicam LC/UV detector yielded a polydispersity of 1.30. Three additional P2VN samples having  $M_v$  equal to 21 000, 180 000 and 265 000 were prepared by solution polymerization with azobis(isobutyronitrile) as initiator<sup>6,7</sup>. The low molecular weight sample was obtained by using carbon tetrachloride as a chain-transfer agent.

All of the polymer hosts used in the photostationary-state fluorescence study were poly(alkyl methacrylate) derivatives: methyl(PMMA), ethyl(PEMA), n-propyl(PnPMA), isopropyl(PiPMA), n-butyl(PnBMA), isobutyl(PiBMA), sec-butyl(PsBMA), tert-butyl(PtBMA), phenyl(PPhMA), isobornyl(PiBoMA), and benzyl(PBzMA). The purification and characterization of these polymers have been previously described<sup>1-3,5</sup>. The background fluorescence of the hosts, checked by photostationary illumination, was typically less than 1% of the fluorescence signal of the P2VN guest polymer.

The blends of P2VN with each of the polymer host matrices were prepared at room temperature by solvent casting from toluene onto microscope slides. Solutions of 50 mg host polymer, 0.15 mg P2VN, and 1 ml of toluene were poured onto the glass slides and allowed to air dry slowly to a constant weight. This procedure led to films with thicknesses of 15–30  $\mu\text{m}$  and residual solvent content of approximately 15%.

All of the solvents used in the low-temperature transient fluorescence study were of spectrograde quality and were obtained from Aldrich. Each of the solvents was vacuum distilled and passed through a silica gel column prior to use. Seven of the seventeen solvents were alkyl benzene derivatives: benzene, toluene, ethylbenzene, n-propylbenzene, *o*-xylene, *m*-xylene and *p*-xylene. Six of them were chlorinated solvents: chloroform, dichloromethane, 1,2-dichloroethane, 1-chlorobutane, chlorobenzene, and 1,2-dichlorobenzene. The remaining four were ethyl acetate, butyl acetate, tetrahydrofuran and pyridine.

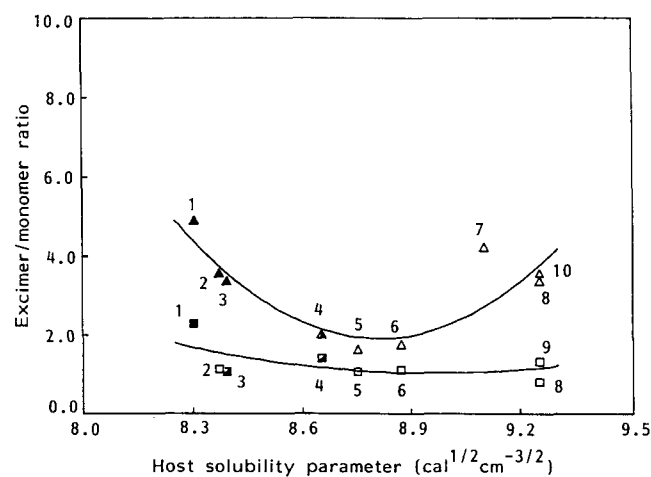
The concentration of the P2VN used for the solution studies was generally less than  $10^{-5}$  M in chromophore units. The solutions were degassed by several freeze pump thaw cycles in a quartz cell equipped with a tightly fitted rubber septum. Special care was taken to minimize the amount of trapped moisture in the sample cell to prevent premature freezing.

**Instrumentation.** Transient fluorescence measurements were performed on a Photochemical Research Associates (PRA), nanosecond time-correlated single photon-counting spectrometer (model 3000). The spectrometer was of conventional configuration utilizing a thyratron-gated, hydrogen-filled flash lamp as the excitation source, Jobin-Yvon excitation and emission monochromators, Hamamatsu R928 Peltier cooled photomultiplier, and Ortec single photon counting electronics. Data were stored on a Tracor Northern TN1750 multichannel analyser and transmitted to a DEC 11/23 minicomputer for analysis.

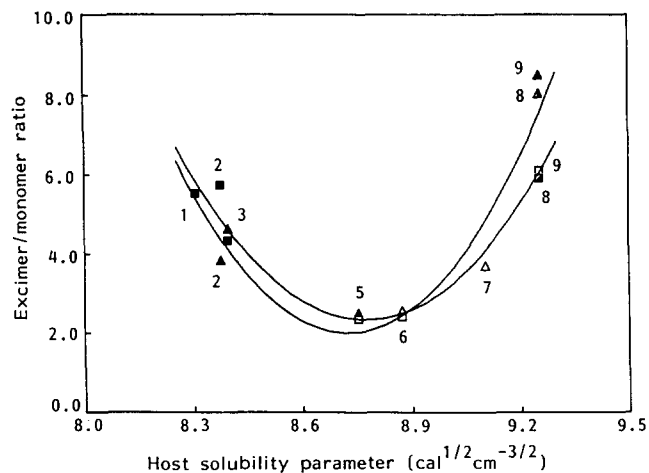
All of the samples were excited at 290 nm with a 10 nm bandpass excitation monochromator filter. P2VN monomer fluorescence, typically observed between 310 nm and 350 nm, was selectively collected with a Toshiba UV340 10 nm bandpass filter. Excimer fluorescence, observed at wavelengths greater than 380 nm, was collected with a Toshiba Y454 10 nm high-pass filter. Instrumental response functions of 1.5 ns fwhm were routinely achieved by collecting the scattered stray light of a Ludox scattering solution at 340 nm, the peak of the monomer emission envelope.

A typical lifetime spectrum consisted of 30 000 counts at the peak channel. The rate of data collection was kept below 3% of the excitation repetition rate to eliminate multiphoton interference. For the low temperature solution runs, the lamp profiles could not be determined during the cooling cycle due to the configuration of the low temperature apparatus. Therefore, only lamp profiles at the start and end of the experiment were averaged. The lamp profile remained satisfactorily constant for the duration of the experiment.

For the low-temperature transient fluorescence measurements, a special arrangement of the components was employed. To minimize moisture build up on the external optics, the entire PRA sample compartment including the monochromators was enclosed in a glove bag. The interior of the glove bag was constantly purged with dry nitrogen and evacuated by a rotary vacuum pump. Dry nitrogen was utilized as the cooling medium. The cooling path involved the passing of a stream of dry nitrogen through copper coils immersed in dewars of liquid nitrogen. The cooled gas was then directed through a heated copper tube and fed into the sample compartment. A Eurotherm digital controller was used in a feedback circuit to monitor the sample temperature and to control the heating rate of the copper tube. A Neslab cold-finger immersion cooler was used to condense moisture within the sample compartment. With this configuration, we could maintain a moisture-free



**Figure 1** The behaviour of  $I_D/I_M$  for 21 000  $M_v$  (squares) and 71 000  $M_v$  (triangles) P2VN dispersed at 0.3 wt% in a series of poly(alkyl methacrylate) hosts as a function of host solubility parameter. The solid lines represent the fitted results of equation (2) to the data. The open, partially filled, and completely filled symbols denote a clear, partially cloudy, and opaque film, respectively. The identification of the hosts is as follows: PiBoMA(1), PiPMA(2), PsBMA(3), PnBMA(4), PnPMA(5), PEMA(6), PS(7), low molecular weight PMMA(8), medium molecular weight PMMA(9), and higher molecular weight PMMA(10)



**Figure 2** The behaviour of  $I_D/I_M$  for 180 000  $M_v$  (squares) and 265 000  $M_v$  (triangles) P2VN dispersed at 0.3 wt% in a series of poly(alkyl methacrylate) hosts as a function of host solubility parameter. The solid lines represent the fitted results of equation (2) to the data. The open, partially filled, and completely filled symbols denote a clear, partially cloudy, and opaque film, respectively. Refer to Figure 1 for the identification of the hosts

environment and control the temperature at 113 K to within 0.1 K accuracy.

The spectrophotometer used for the photostationary-state fluorescence study has been described previously<sup>4-9</sup>. The cast films were left on the glass slides and fluorescence measurements were taken with front-face illumination at an excitation wavelength of 290 nm. This method of sample examination was required because several of the samples were very brittle. After each spectrum was completed, the slide was translated to expose a different portion of the film; in this manner seven to nine spectra of each film were obtained. The reported  $I_D/I_M$  in Figures 1 and 2 is an average of the results obtained from all spectra of each film.

**Analysis.** Simple intensity ratios taken in positions of minimum overlap were used for the photostationary-state fluorescence spectra, with the excimer intensity being measured at 398 nm and the monomer intensity at 337 nm.

The transient fluorescence profiles were fitted with the model trial function by the method of iterative deconvolution with the lamp profile using a non-linear  $\chi^2$  minimization algorithm of Marquardt<sup>13</sup>. The quality of fit was judged by the reduced  $\chi^2$  criterion, visual inspection of the deviations in the weighted residuals, and the profile of the autocorrelation function. The Hamamatsu R928 photomultiplier used in our system exhibited a relatively small wavelength dependence in the range shaded. Therefore, no corrections for the energy-dependent time shift of the photomultiplier were required.

## RESULTS

### *P2VN dispersed in poly(alkyl methacrylate) host matrices*

Interpretation of the photophysical behaviour of blends containing an aryl vinyl polymer requires that consideration be given both to the nature and concentration of the trap, the excimer forming site, and to

the energy migration process by which those traps are sampled. We first examine the trap.

There are three different types of excimer-forming sites in aromatic vinyl polymers. Excimer formation from the intramolecular association between adjacent repeat units is independent of chain concentration. Frank and Harrah<sup>20</sup> proposed earlier that only the meso dyad configuration will contribute appreciably to adjacent intramolecular EFS. Subsequent determination of the conformational energy maps for PS by Yoon *et al.*<sup>21</sup> confirmed this proposal. Moreover, Flory<sup>22</sup> has shown that modest changes in the radius of gyration of an individual coil, such as those due to chain expansion in a good solvent, will not be felt at the level of the local dyadic population. Therefore, the small number of adjacent intramolecular EFS should be independent of the host matrix.

The second type of EFS arises from the association between aromatic rings from remote segments of the same chain due to the contiguous chain bending back upon itself. The population of these non-adjacent intramolecular EFS would increase as the radius of gyration of the random coil decreases in a thermodynamically poorer host matrix. Since the interaction is still intramolecular, the non-adjacent intramolecular EFS is also independent of chain concentration.

The intermolecular EFS is formed between segments of different chains and is therefore dependent on guest polymer concentration. If the guest and host polymers are miscible, the guest chains will be placed in a random fashion within the host matrix. For immiscible blends, clustering of the guest molecules will occur, and the extent of this aggregation will depend on the thermodynamic nature of the guest/host interaction.

In addition to considering the effects on  $I_D/I_M$  from the population of the different types of EFS, we must also address the role of electronic energy transport among the intramolecular and intermolecular chromophores. For dilute, molecularly dispersed blends, the guest coils should be isolated and EET is expected to occur mainly in a one-dimensional fashion along the contour of the chain. Depending on the rate of energy migration and the molecular weight of the coil, only portions of the coil will be sampled by exciton hopping. If the thermodynamic conditions are altered towards immiscibility, the radius of gyration of the coil will be reduced and the population of non-adjacent intramolecular EFS could increase. Even if there is no macroscopic phase separation, there are two possible photophysical consequences. First, if EET is efficient enough to sample the entire coil, more traps will be accessible and  $I_D/I_M$  will increase. Second, if the 'backbending' leads to sufficiently close approach of remote aromatic rings such that alternative short-circuit pathways are formed for the migrating exciton to transfer across loops,  $I_D/I_M$  will also increase<sup>23</sup>.

In the case of concentrated blends, phase separation will often result. The subsequent increase in  $I_D/I_M$  is directly proportional to the local guest polymer concentration due to an increase in the number of intermolecular EFS. In contrast to the intramolecular case, the role of EET is more subtle. The most important situation is probably in the incipient stages of phase separation where one would expect an increase in the dimensionality of EET, with a consequent increase in efficiency of sampling.

The complex interplay between polymer photophysics and polymer morphology may be demonstrated by the photostationary results for the four different molecular weight P2VN samples blended at 0.3 wt% with the poly(alkyl methacrylate) hosts, which are presented in *Figures 1* and *2*. Here  $I_D/I_M$  has been plotted against the solubility parameter of the polymer hosts, obtained from Barton<sup>24</sup>. The solubility parameter was first used to correlate the photophysical behaviour of polymer blends by Frank and Gashgari<sup>1-3</sup>. Its usage was motivated by the prediction of regular solution theory that the binary interaction parameter may be described by:

$$\chi_{12} = \frac{V_r}{RT} (\delta_1 - \delta_2)^2 \quad (1)$$

where  $V_r$  is a reference volume, taken to be the smaller of the repeat unit molar volumes for the two blend components,  $\delta_i$  is the Scatchard-Hildebrand solubility parameter for the  $i$ th component in the blend, and  $R$  is the gas constant.

For each of the P2VN molecular weights, a smooth curve can be drawn through the  $I_D/I_M$  results, with the minimum occurring near  $\delta_{P2VN} = 8.85$ , the value originally found by Frank and Gashgari<sup>1</sup>. Even though there is a moderate variation in host molecular weights over the homologous series, there is no appreciable deviation from the smooth curve behaviour. As the P2VN molecular weight increases, the curvature of the smooth curve becomes more concave upwards. The rate of increase in  $I_D/I_M$  is greater for blends in which there is a larger difference between the guest and host solubility parameters.

The smooth curves of *Figures 1* and *2* arise from application of the following fitting function:

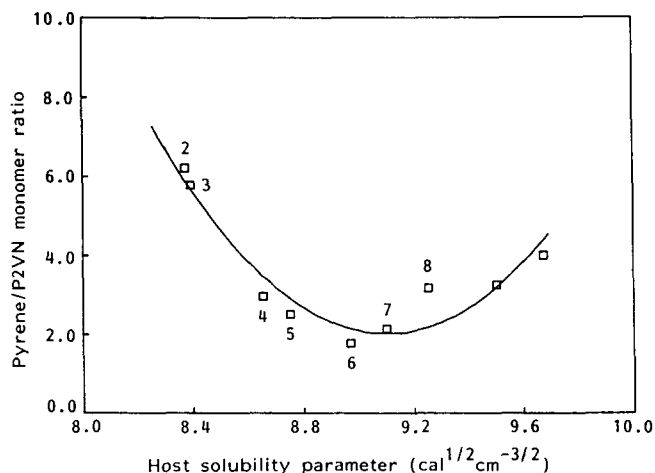
$$I_D/I_M = A + B(\delta_{\text{host}} - \delta_{P2VN})^2 \quad (2)$$

where  $A$  and  $B$  are arbitrary fitting constants. Rather than specifying the solubility parameter of P2VN to be the value deduced from the results of Frank and Gashgari's earlier study<sup>1</sup>, we treat it as a fitting parameter in order to see the influence of P2VN molecular weight. The results of a non-linear regression fit of equation (2) to the fluorescence data are summarized in *Table 1*.

Under normal experimental conditions it is difficult to separate the effect of changing EFS concentration from the effect of changing efficiency of EET. Use of a different donor-trap system, however, affords the possibility of separating these two effects. Specifically, we utilize the same host series with a P2VN guest polymer containing covalently bound pyrene (Py) groups at the chain ends. In this end tagged Py-P2VN-Py system, the naphthalene units along the chain contour serve as donors, while the Py rings become traps. The main difference between this guest polymer and the normal untagged P2VN monomer-excimer system is that the number of pyrene rings is physically fixed; hence, the number of this type of

**Table 1** Summary of the fitting parameters of equation (2)

Guest (molecular weight)	$A$	$B$	$\delta_{P2VN}$
P2VN (21 000)	1.03	1.52	8.95
P2VN (71 000)	1.90	9.50	8.81
P2VN (180 000)	2.33	16.01	8.77
P2VN (265 000)	1.99	19.45	8.72
Py-P2VN-Py (30 000)	2.02	7.25	9.10



**Figure 3** The ratio of pyrene trap fluorescence to P2VN monomer fluorescence as a function of host solubility parameter. The solid curve represents the fitted results of equation (2) to the data. Refer to *Figure 1* for the identification of the hosts

energy trap is constant for all the blends with the poly(alkyl methacrylate) hosts. Any change in the measured Py trap fluorescence must be due to changes in the pathway and efficiency of EET, which reflect intramolecular changes in the configuration of the P2VN coil.

The pyrene-tagged P2VN polymer had a molecular weight of about 30 000. It was blended with the poly(alkyl methacrylate) hosts (0.3 wt%). An analogous photophysical measurement for these blends is the ratio of Py trap fluorescence to naphthalene monomer fluorescence,  $I_T/I_M$ . This parameter is plotted as a function of host solubility parameter in *Figure 3*. Since the number of Py tags is small, we would expect the Py-P2VN-Py to have the same thermodynamic and structural properties as normal P2VN of comparable molecular weight. *Figure 3* shows that the fluorescence of the 30 000  $M_v$  Py-P2VN-Py blends is qualitatively the same as the normal P2VN blends; a broad U-shaped smooth curve can be drawn through the data with the minimum centred around the point where the guest and host solubility parameters are similar.

#### P2VN dispersed in glassy monomeric solvent matrices

Fredrickson and Frank (FF)<sup>19</sup> have developed a model for EET between donors and traps in solutions of an aryl vinyl polymer. This model is an improvement over an earlier treatment of one-dimensional energy migration by Fitzgibbon and Frank<sup>11</sup> in that it allows contributions from both singlet energy migration and segmental rotation to the excimer formation process. The rate of rotation, however, is assumed to be much slower than migration, so that the primary effect of segmental rotation will be to trap directly the excitation during its residence on a particular monomeric chromophore without disturbing the equilibrium trap population. The FF model shows that in the presence of EET, the transient fluorescence decay profiles usually result in a non-exponential form, even for the simplest of kinetic schemes. The process can be described adequately by a transfer rate function<sup>25</sup>, i.e. a function of time, which reflects the distribution of all the pertinent decay pathways available for monomer and excimer deactivation. Associated with

each of these pathways, or modes, is a characteristic decay time that does not correspond to the exponent lifetime of any of the excited states participating in the kinetic scheme.

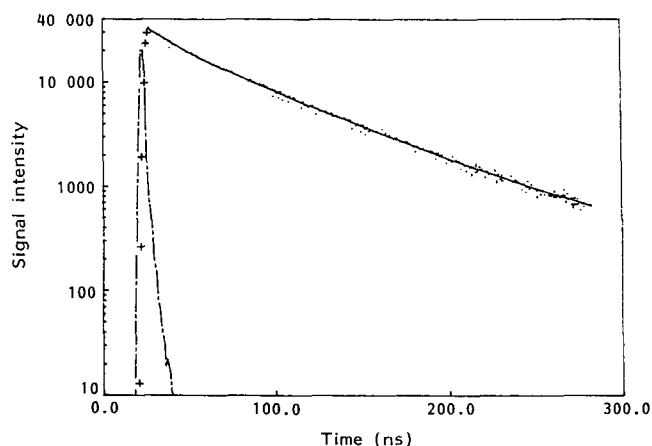
Fredrickson and Frank<sup>19</sup> obtained expressions for the monomer response function,  $i_m(t)$ , valid for small EFS trap concentrations,  $q \ll 1$ , and long times,  $tW > 1$

$$i_m(t) = Q_{im} k_m (1-q)^2 \times \exp[(4q^2 W - k_m - k_{rot})t] \operatorname{erfc}[2q(Wt)^{1/2}] \quad (3)$$

where  $Q_{im}$  is the quantum efficiency for monomer fluorescence. The rate constant  $k_m$  includes the total rate of monomer decay by radiative and non-radiative pathways in the absence of energy migration and rotational sampling. The rate constant  $k_{rot}$  represents the rate at which an excited monomer is transformed into an excimer by segmental rotation. The sum of the two rate constants equals the inverse of the lifetime,  $\tau$ , for monomer deactivation in the absence of EET. The quantity  $W$  represents the rate constant for nearest neighbour EET between two donor chromophores, averaged over the transition moment orientation and interchromophore separation associated with each rotational dyad. The equilibrium excimer trap fraction,  $q$ , includes both intramolecular and intermolecular, adjacent and non-adjacent EFS, and is highly dependent on the temperature of the dilute polymeric solution and the miscibility of the P2VN in the host matrices. The conformationally averaged EET rate constant,  $W$ , and the magnitude of  $q$  will determine a set of dominant modes for monomer decay.

A typical transient monomer fluorescence decay profile of P2VN in n-propylbenzene, representative of all the low-temperature solution results, is presented in *Figure 4*. The intensity of P2VN monomer emission, normalized to 30 000 counts, is plotted as a function of decay time after the initial excitation. (The broken curve, with a fwhm of 1.5 ns, represents the excitation profile of the lamp pulse. The monomer decay curve is represented by the individual dots with a typical time resolution of 1.25 ns per channel.)

The solid curve in *Figure 4* represents a fit of equation (3) to the transient fluorescence results. A summary of the



**Figure 4** The transient fluorescence decay for 71000  $M_v$  P2VN dispersed at low concentration in n-propylbenzene at 113 K. The solid line is a fit of the Fredrickson and Frank model for one-dimensional EET to the results

**Table 2** Rate of EET in P2VN dispersed at low concentration in a series of monomeric glassy solvents

No.	Solvent	$\delta$ (cal <sup>1/2</sup> cm <sup>-3/2</sup> )	$W^{-1}$ (ns)	$\chi^2$
1	1-chlorobutane	8.39	322	1.02
2	Butyl acetate	8.59	298	1.20
3	n-propyl benzene	8.64	320	1.01
4	p-xylene	8.77	308	1.03
5	Ethyl benzene	8.79	273	1.05
6	m-xylene	8.82	281	1.03
7	Toluene	8.91	285	1.01
8	o-xylene	8.99	272	1.05
9	Ethyl acetate	9.02	202	1.15
10	Benzene	9.16	251	1.02
11	Chloroform	9.23	245	1.07
12	Tetrahydrofuran	9.38	205	1.10
13	Chlorobenzene	9.56	191	1.03
14	Dichloromethane	9.80	223	1.07
15	1,2-dichloroethane	9.81	235	1.08
16	1,2-dichlorobenzene	10.04	266	1.03
17	Pyridine	10.62	295	1.13

fitting constants for all of the solvents is presented in Table 2. Gelles and Frank<sup>8,9</sup> have determined the intramolecular excimer trap fraction,  $q$ , to be 0.026 for PS at 300 K from Monte-Carlo simulation based on known statistical weight distribution of the different conformational dyads of the polymer chain. Furthermore, they have found that the excimer trap fraction may be described by a Boltzmann relation, with an effective equilibrium EFS energy of 1.7 kcal mol<sup>-1</sup>. The conformational energy map and configurational statistical weight distribution for P2VN are quite similar to those for PS. Therefore, we have used a value of  $q$  equal to 0.026 for P2VN at 300 K and calculated the decrease in the dyad trap fraction as a function of decreasing temperature based on the same value of the effective site energy.

## DISCUSSION

### P2VN dispersed in poly(alkyl methacrylate) host matrices

We can now propose a model to describe the behaviour of  $I_D/I_M$  for the different molecular weight P2VN samples in the poly(alkyl methacrylate) hosts. We begin by examining the dependence of the parameter  $A$ , the value of  $I_D/I_M$  for which  $\Delta\delta$  equals zero, on molecular weight of P2VN. For dilute blends in which  $\Delta\delta$  equals zero, the P2VN coil should be expanded and it is reasonable to approximate the excitation migration process as a one-dimensional random walk along the chain as done earlier by Fitzgibbon and Frank<sup>11</sup>. For short chains, there is only a small probability of finding a trap due to the low trap concentration; indeed, for very short chains there may be few if any EFS traps at all and  $I_D/I_M$  will be very small. An increase in the molecular weight will yield more distinct sites available for sampling so that the probability of finding a trap will increase, and  $I_D/I_M$  will increase.

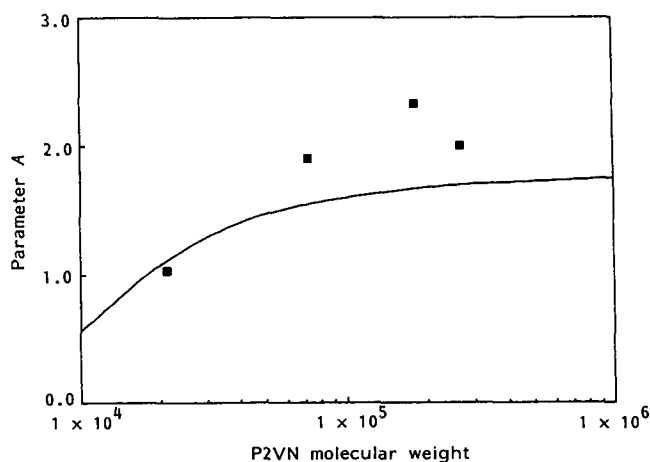
The  $I_D/I_M$  ratio levels off at higher molecular weights for two reasons. The first is that the lifetime of the excitation is finite so that the length of the chain that can be sampled is limited. This effect is enhanced by the inefficiency of a one-dimensional random walk resulting from the re-sampling of sites. The number of distinct sites visited in  $n$  steps for a one-dimensional walk without emission and traps is proportional to  $n^{1/2}$ . The second

reason is that the trap concentration is finite. This has the effect of dividing the chains into shorter segments, thus making long chains appear photophysically similar to lower molecular weight chains.

The one-dimensional EET model was employed by Gelles and Frank<sup>8,9</sup> to explain the molecular weight dependence of excimer fluorescence from PS dispersed in poly(vinyl methyl ether) (PVME). This is a particularly good system to study because it has been conclusively shown that the PS/PVME blend prepared by solvent casting from toluene is miscible in all proportions. PS molecular weights ranging from 1000 to 350 000 were used, and the  $I_D/I_M$  results were fitted quite well by the one-dimensional EET model. Thus, the PS/PVME results could serve as a reference point with which to compare the P2VN ( $\Delta\delta=0$ ) blends.

The basis for this comparison is two-fold. First, the similarity in the statistical configuration maps and the quantum yield ratios between P2VN and PS suggest the same photophysical behaviour from the two guests relative to thermodynamic variations of the host surrounding<sup>21</sup>. Second, changes in  $I_D/I_M$  for the PS/PVME blend as a function of guest molecular weight directly reflect modification in the efficiency of intramolecular EET. Gelles and Frank observed a 30% increase in  $I_D/I_M$  corresponding to an order of magnitude increase in the guest molecular weight from 10 000 to 100 000 for 5% PS dispersed in PVME at 298 K. By contrast, there is nearly a 300% increase in  $I_D/I_M$  for P2VN in the poly(alkyl methacrylate) hosts over the same molecular weight range.

The solid curve in Figure 5 represents the behaviour of  $I_D/I_M$  as a function of guest molecular weight as predicted by the one-dimensional EET model of Fitzgibbon and Frank. In this calculation, the fraction of EFS dyads in the guest is taken to be 0.026 and the ratio of the one-dimensional EET rate to the overall monomer decay rate is taken to be 5900. For the 21 000  $M_v$  P2VN, there is a very good match between the experimental  $I_D/I_M$  and the one-dimensional EET model prediction. At this low molecular weight, the P2VN chains are isolated and extended, and energy migration proceeds intramolecularly between adjacent chromophores.



**Figure 5** The behaviour of  $I_D/I_M$  as a function of P2VN molecular weight for blends in which the difference between the guest and host solubility parameters approaches zero. The solid curve is that predicted by the one-dimensional EET model by Fitzgibbon and Frank. Local phase separation is suspected to occur for guest molecular weights greater than 20 000  $M_v$ .

The deviation in  $I_D/I_M$  from the one-dimensional prediction for P2VN  $M_v$  greater than perhaps 30 000–40 000 suggests a change in the efficiency of EET in the higher guest molecular weight blends. This can arise from two physical phenomena. The first possibility is small-scale phase separation in the high molecular weight blends. This results in an increase in the efficiency of EET due to the addition of intermolecular pathways. Semerak and Frank<sup>4,10</sup> have found local phase separation occurring in blends of high molecular weight P2VN with PS host matrices. The second possible explanation is that it is due to local coil contraction, which increases the efficiency of intramolecular EET. In both cases, the dimensionality of EET will increase, resulting in enhanced sampling of the excimer traps.

As the thermodynamic interaction between the guest and host is altered towards incompatibility, we note several changes in  $I_D/I_M$  as functions of both guest molecular weight and host solubility parameter for a given P2VN molecular weight. For lower molecular weight P2VN, the increase in  $I_D/I_M$  with the difference between guest and host solubility parameters is much more gradual, as seen in *Figure 1*. The small increase in  $I_D/I_M$  as  $|\Delta\delta|$  increases, in the case of 21 000  $M_v$  for example, is possibly due to the increase in the local intramolecular chromophore density accompanied by an increase in the efficiency of EET and pathways for enhanced EFS sampling.

From the Py–P2VN–Py results in *Figure 3*, it appears that the change in the fluorescence of the Py–P2VN–Py guest in the various host matrices reflects changes in the efficiency in EET. Decreasing the thermodynamic compatibility between the guest and host serves to compress the Py–P2VN–Py coil. Bending back of portions of the chain and increasing the proximity of non-adjacent chromophores provide additional pathways for EET and enhance the sampling of the Py traps. Ng and Guillet<sup>26</sup> have studied the nature of EET in polymer molecules with the chain ends selectively tagged with chromophoric traps. In solid solutions, the transfer of singlet energy from the donor chromophores along the chain to the acceptors at the chain ends proceeds primarily through nearest neighbour one-dimensional EET followed by a one-step downhill transfer to the trap. In fluid solutions, segmental diffusion and rotation enhance the rate of both migration and single-step transfer and subsequently improve the overall transfer rate and efficiency. Lowering the solvent quality has essentially the same effect in raising the rate of EET.

Frank and Gashgari<sup>2,3</sup> have studied the effect of P2VN guest concentration up to 8 wt % on  $I_D/I_M$  for blends with PMMA (80 400, 125 400, and 163 400), PEMA (395 000), and PnBMA (254 400), the same host matrices included in the present work. They separated the observed  $I_D/I_M$  into an intramolecular part, corresponding to the value of  $I_D/I_M$  at very high dilution, and an intermolecular part. The latter contribution was the focal point for a phenomenological clustering model. Their model empirically describes the two possible forms of intermolecular interaction giving rise to excimer formation: chain clustering due to random mixing in a concentrated miscible system and local enhancement of chromophore density due to domain formation during phase separation.

In this model, a reference volume  $V_0$  surrounding the excited chromophore is defined such that it encloses all

possible aromatic rings that can be sampled by EET during the lifetime of the excited state. In the case of moderately concentrated solid solutions, the reference volume will include segments from different guest chains. A similar effect results if phase separation takes place such that the local concentration of the guest polymer chains within a separate domain is much higher than the nominal bulk concentration. If the guest and host polymers are completely miscible, the distribution of guest chain segments within  $V_0$  will be random. For this uniform mixing case,  $I_D/I_M$  is proportional to the bulk concentration of the guest polymer. If the blend components are thermodynamically incompatible, phase separation will occur and a substantially higher guest concentration is located within  $V_0$ .

Frank and Gashgari found that the intermolecular contribution to  $I_D/I_M$  could be fitted quite well by an expression of the form  $I_D/I_M(\text{intermolecular}) = (\alpha + \beta M_{\text{host}} \chi_{12})C$ , where  $\alpha$  and  $\beta$  are constants,  $M_{\text{host}}$  is the host molecular weight,  $\chi_{12}$  is the binary interaction parameter, and  $C$  is the P2VN bulk concentration. The first term arises from random mixing, whereas the second is due to inhomogeneous clusters; the second term is about five times larger than the first<sup>3</sup>. It is important to note that this phenomenological expression is for a particular P2VN molecular weight, which is smaller than the molecular weight of any of the host polymer matrices.

The use of the product of molecular weight (or degree of polymerization,  $N$ ) and the interaction parameter to characterize the degree of incompatibility has its roots in classical Flory–Huggins lattice theory of polymer solutions as well as more recent treatments of statistical thermodynamics. For example, prediction of the plait point concentrations of polymer A, polymer B, and solvent in a ternary system depends strongly on the  $N\chi$  product. Moreover, Leibler<sup>27</sup> has demonstrated in several sophisticated statistical mechanics treatments of blends of homopolymers and of homo- and copolymers that the  $N\chi$  product was the only parameter that had an appreciable effect on the phase behaviour.

In a separate paper of this series<sup>28</sup> we have extended the cluster model to account for the effects of the molecular weights of both the host and guest polymers. The intermolecular contribution to  $I_D/I_M$  for a particular (low) bulk concentration of P2VN has been shown to be of the form

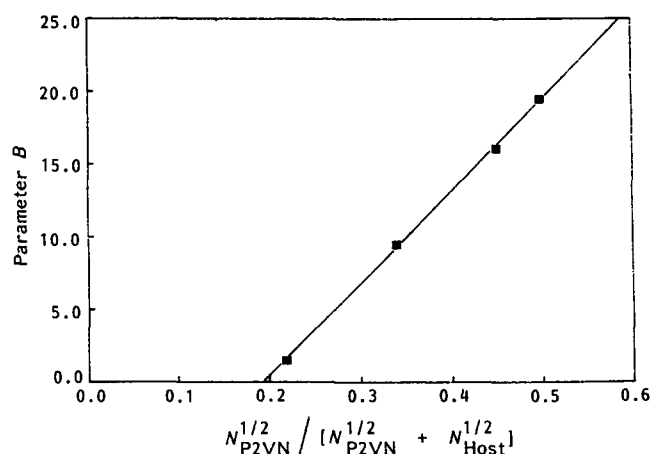
$$\frac{I_D}{I_M}(\text{intermolecular}) = \gamma N_{\text{host}} \chi_{12} \left[ \frac{N_{\text{P2VN}}^{1/2}}{N_{\text{P2VN}}^{1/2} + N_{\text{host}}^{1/2}} \right] \quad (4)$$

where  $N_i$  is the degree of polymerization and  $\gamma$  is a proportionality constant. Basically, this treatment introduces a new quantity, the term in brackets, which represents the relative concentration of the P2VN guest compared with the host at the plait point of the ternary solvent casting system.

A possible way of testing this modified cluster model is with the  $B$  parameter of *Table 1*. From equation (2) it is clear that  $B$  should be proportional to the product

$$B \propto \gamma N_{\text{host}} \left[ \frac{N_{\text{P2VN}}^{1/2}}{N_{\text{P2VN}}^{1/2} + N_{\text{host}}^{1/2}} \right] \quad (5)$$

Although the host polymers examined in the present study cover a range of molecular weights, we will take an average value of  $M_{\text{host}} = 200\,000$  and  $N_{\text{host}} = 1750$ . *Figure 6* shows the dependence of  $B$  on the bracketed quantity of



**Figure 6** The linear dependence of the fitted parameter  $B$  according to equation (5) demonstrates that the modified cluster model, represented by equation (4), is capable of describing the photophysical behaviour of incompatible blends. The bracketed term in equation (4) denotes the relative concentration of the P2VN guest compared with the host at the plait point of the ternary solvent casting system

equation (5). The agreement is excellent, demonstrating that the modified cluster model is capable of describing these incompatible blends quite well.

An interesting extension of this approach is to examine the value of the bracketed term in equation (5) at which  $B$  vanishes. According to equation (2) this should correspond to the point where all intermolecular interactions in these dilute blends vanish. This occurs at  $M_{P2VN} = 15\,800$ , as shown in *Figure 6*. This suggests that miscible systems may be obtained for low concentration (0.3 wt %) blends with these high molecular weight host polymers only as long as the P2VN molecular weight is less than 15 800. In fact, Semerak and Frank<sup>4,10</sup> have shown that microphase separation does occur for blends of P2VN (21 000) with PMMA (100 000). It does not appear to occur, however, when P2VN (21 000) is blended with PS, a more compatible polymer host.

#### *P2VN dispersed in low temperature solid solvent matrices*

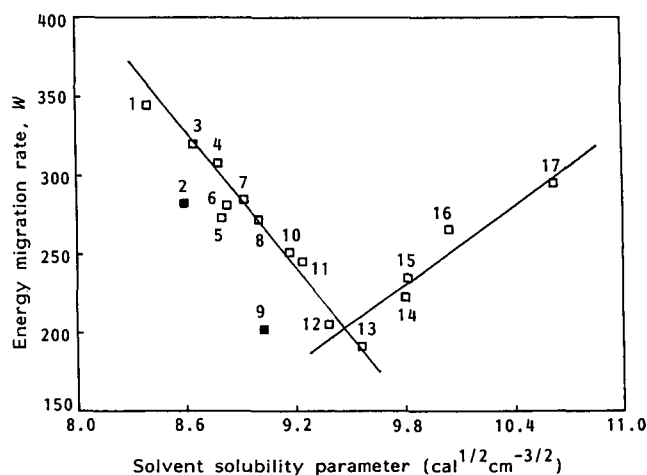
In the previous papers<sup>1-14</sup> on vinyl aromatic polymers blended with poly(alkyl methacrylate) hosts, the influence of the solvent casting process on the morphology and the observed fluorescence for the blends was recognized but not extensively studied. As the solvent in the matrix evaporates, the mobilities of both guest and host polymers are reduced such that an overall blend morphology will eventually be 'frozen-in'. This final blend morphology will be more representative of the ternary blend thermodynamics at the point of freeze-in rather than that of a binary blend. For high molecular weight blends, it is conceivable that phase separation can occur early in the drying process. We have considered this point in some detail recently<sup>29</sup>. If so, it might be difficult to isolate intramolecular photophysical events such as the role of EET in sampling the intramolecular EFS during coil contraction. The relative contribution of EET may be clarified however, by detailed consideration of changes in the efficiency of EET in a system where intermolecular phase separation and intramolecular coil contraction can be separated.

A host matrix series composed of monomeric glassy solvents provides a good system with which to study

changes in the efficiency of EET as the intramolecular configuration of a dilute guest chain is modified. In the glass the segmental motion is drastically reduced, thus fixing the EFS concentration. In addition, there is a higher probability that the P2VN will remain molecularly dispersed in the glassy solvent as opposed to the polymeric matrix prepared by solvent casting. We will assume for a given P2VN molecular weight at a constant temperature of 113 K that the amount of coil contraction due to the low temperature is constant for the different solvents. Therefore, further changes in the coil dimension, which should be manifested by changes in the efficiency in EET, can be attributed to variation in the thermodynamic compatibility between P2VN and the solvent host matrix.

The FF<sup>19</sup> model provides a straightforward method to determine the efficiency of energy migration among the frozen array of chromophores from transient fluorescence profiles. *Figure 7* illustrates the change in  $W$  as a function of the solvent solubility parameter. The behaviour of  $W$  yields the same qualitative shape as  $I_D/I_M$  relative to the thermodynamic compatibility between the guest and host. As the difference between the guest and host solubility parameters increases, the rate of energy migration increases. This is consistent with the explanation that the dimension of the guest coil contracts leading to a decrease in the average chromophore separation. The fact that the chains are isolated removes the possibility of intermolecular aggregation. Therefore, it is likely that the change in  $W$  directly reflects the difference in coil expansion in the solvents.

Another interesting feature of the results in *Figure 7* is the uniformity of  $W$  for both the alkylbenzene and chlorinated solvents. The polar and hydrogen-bonding interactions in these two groups of solvents are quite different. It seems, however, that the conformation of the P2VN coil is not sensitive to these different local interactions. With the exception of the two ester solvents,  $W$  is symmetric with regard to the solubility parameter difference. The value of the solubility parameter at the point of intersection of the solid lines of *Figure 7* is about  $9.5 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ , which corresponds to an estimate of  $\delta$  for 71 000  $M_v$  P2VN in this group of aromatic and chlorinated solvents<sup>4,10</sup>.



**Figure 7** The rate of EET in 71 000  $M_v$  P2VN dispersed at low concentration in a series of monomeric glassy solvents. The filled symbols correspond to the two ester solvents which consistently yielded lower values of  $W$ . The identification of the solvent hosts is summarized in *Table 2*

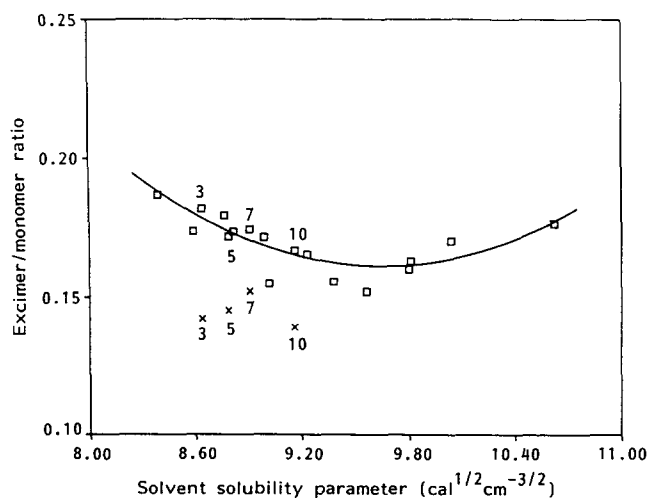


The difference between this value of  $\delta=9.5$  at the minimum and that observed in the poly(alkyl methacrylates), 8.85, arises from the different chemical characteristics of the hosts. This effect has been observed previously<sup>4</sup>, and simply demonstrates that the single component solubility parameter is only an approximate guide to represent the segment-segment interactions. Some indication of this fact from these results is that the two ester solvents are shifted to lower values of  $\delta$  than the aromatic or chlorinated solvents. In general,  $\delta_{P2VN}$  may not be the same if measured in another homologous host series having widely differing dispersive, polar, or hydrogen bonding interactions. Li *et al.*<sup>18</sup> observed similar behaviour for PS with random pyrene tags in similar solvents at room temperature.

The fact that the mathematical form of equation (3) fits the transient fluorescence profiles does not necessarily mean that EET is indeed strictly one-dimensional between nearest neighbour chromophores. Such a situation would only arise for highly extended P2VN chains, which is unlikely to be the case for these low temperature solvent glasses. For isolated polymer coils in this study, higher dimensionality in EET is likely due to cross-loop hopping of the exciton among non-adjacent chromophores along the chain contour. Our results indicate, however, that the dominant pathway of EET in P2VN in a series of alkylbenzene and chlorinated solvents at low temperatures is one-dimensional in nature.

A verification of the applicability of the FF model in describing EET in dilute solutions of P2VN at low temperatures would be to compare the calculated values for  $I_D/I_M$  from the fitted parameters of the model with those independently measured in a photostationary-state excitation experiment. For a photostationary-state fluorescence experiment with one type of excited monomer and one excimer trap, Fredrickson and Frank integrated equation (3) as a function of time to obtain an expression for  $I_D/I_M$

$$\frac{I_D}{I_M} = \frac{Q_{fe}}{Q_{fm}} \times \left[ \frac{k_{rot}/k_m + 2q[1 + (W/k_m)^{1/2}(1 + k_{rot}/k_m)^{1/2}] - q^2}{(1-q)^2} \right] \quad (6)$$



**Figure 8** A comparison of experimental  $I_D/I_M$  for P2VN in several aromatic solvents (crosses) with  $I_D/I_M$  calculated from equation (6) (squares). The solid curve is a fit of equation (2) to the calculated results. The solvents are n-propylbenzene(3), ethylbenzene(5), toluene(7), and benzene(10)

The values of  $I_D/I_M$  for 71000  $M_v$  P2VN at 113 K, calculated from equation (6) for each of the solvents, are plotted in *Figure 8* as a function of solvent solubility parameter. A value of 0.42 is taken for the ratio of excimer to monomer quantum yields<sup>12</sup>. The value of the rate constant  $k_m$ , which corresponds to the sum of the rate constants for radiative and non-radiative deactivation of the monomer, is estimated by measuring  $k_m$  of 2-ethylnaphthalene, a model compound for P2VN, in the solvents at 113 K. Several features of *Figure 8* are worth noting. The general shape of the data is similar to that of the different molecular weight P2VN dispersed in the poly(alkyl methacrylate) hosts. Fitting the data with equation (2) yields a value of  $9.62 \text{ cal}^{1/2} \text{ cm}^{-3/2}$  for  $\delta_{P2VN}$ . The values of  $I_D/I_M$  for the ester solvents have been excluded in the fit because they seem to deviate from the regular trend.

The  $I_D/I_M$  of P2VN in toluene, benzene, ethylbenzene, n-propylbenzene, and n-butylbenzene have been independently measured in photostationary-state excitation experiments at 113 K. The results are represented by filled symbols in *Figure 8*, and their corresponding counterparts calculated from equation (6) are identically labelled. Fairly good agreement is found between the photostationary-state fluorescence  $I_D/I_M$  and those estimated from the FF model. This suggests that the FF model is indeed applicable for treating EET in P2VN in glassy solution. Furthermore, it lends support to the proposal that increase in the efficiency of EET is due mainly to coil contraction when the thermodynamic compatibility between the guest and host is altered towards immiscibility.

## SUMMARY

The different poly(alkyl methacrylate) hosts have provided an environment in which the configuration and morphology of the guest P2VN polymer can be modified by changing the thermodynamic compatibility of the blend. The increase in  $I_D/I_M$  with increasing P2VN molecular weight can be rationalized by a one-dimensional EET model developed by Fitzgibbon and Frank, which attributes the increase in  $I_D/I_M$  to an extension of the range of EFS sampled by EET. The results also suggest the possibility of small-scale phase separation or local coil contraction for P2VN with  $M_v$  greater than 20000.

As the  $\Delta\delta$  is increased, we observed an increase in  $I_D/I_M$  that can be attributed to either phase separation or coil contraction leading to both an increase in the local EFS population and in the efficiency of EET. In either case, the average chromophore separation is lowered and EET can become quasi-one-dimensional in nature. The cross-loop hopping and interchain short-circuiting allows the enhanced sampling of EFS by the migrating exciton leading to an increase in  $I_D/I_M$ .

To investigate the efficiency of intramolecular EET relative to the enthalpic interaction between the guest and host and independent of intermolecular effects such as phase separation, we chose a host series composed of monomeric glassy solvents. The results indicate that the efficiency of one-dimensional EET is directly related to the configuration of the P2VN coil, which in turn is related to the thermodynamic compatibility of the binary

blend. The model by Fredrickson and Frank proves useful in treating EET in dilute solutions of P2VN at low temperature.

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