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Molecular Weight Dependent Emission Properties of Poly(*N*-vinylcarbazole) in Polymer Blends

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ABSTRACT: The emission properties of poly(*N*-vinylcarbazole) (PVK), serving as a guest in films of polystyrene (PS) and poly(methyl methacrylate) (PMMA), have been investigated. Under these conditions, the steady-state fluorescence spectra and fluorescence decay times of PVK are observed to be molecular weight dependent. The ratios of fluorescence intensities measured at wavelengths within the two characteristic excimer fluorescence bands of PVK are found to be proportional to $\bar{M}_n^{\alpha}$, where $\bar{M}_n$ is the number-average molecular weight of the PVK and α is a parameter whose value is dependent on the host polymer. These molecular weight dependent emission properties are a consequence of energy migration along isolated PVK chains or within microdomains to preformed excimer sites serving as traps. The two values of α obtained are shown to be related to the PVK chain dimensions in the respective host polymers and, thus, to this extent, can be considered to be a measure of the degree of compatibility of the PVK guest with the two different host polymers. The two values of α are shown to be consistent with other properties of these films generally considered to be measures of polymer blend compatibility and indicate that PVK exhibits a greater degree of compatibility with PS than with PMMA.

Introduction

Interest in the complex photophysical properties of macromolecules, both synthetic and biological, has expanded rapidly in recent years.[1] This has been the result of an ever-increasing recognition on the part of polymer scientists of the versatility and sensitivity of luminescence measurements in probing a variety of phenomena in polymer systems. The majority of these investigations have been designed to probe the nature of the electronic states in polymers as revealed through their fluorescence and phosphorescence properties; however, more recent developments have turned toward the utilization of luminescent measurements to probe polymer structure and dynamic structural changes over a wide spectrum of relaxation rates.[2]

Vinyl polymers containing aromatic pendant groups, because of the diversity of photophysical properties they display, have received by far the most attention. For example, solutions of many aromatic pendant group vinyl polymers display, in addition to the monomer-like fluorescence characteristic of the isolated pendant group, a new structureless emission band at lower energies. The new emission band results from the formation of an excited-state complex, termed an excimer, in which two pendant chromophores, one of which is electronically excited, achieve a coplanar sandwich-like geometry.[3] In this regard, the emission properties of vinyl aromatic polymers are similar, in certain respects, to the concentration-dependent emission spectra observed from solutions of many aromatic monomer species. In the case of polymers, however, the emission properties are generally independent of concentration, at least over the range of concentrations where interchain interactions are unimportant. The existence of excimer fluorescence is a consequence of the high local concentration of pendant groups and reflects on the configurational and conformational aspects of the polymer chain as well as the efficiency of energy migration along the chain.

The existence of excimer fluorescence in polymer systems has been recognized as a particularly useful probe with which to address a wide variety of problems in polymer science through the use of luminescence methods. For example, Winnik and co-workers used excimer fluorescence in an elegant manner to investigate the molecular weight dependence of end-to-end cyclization in polystyrene by end-capping the polymer with pyrene.[4] Excimer fluorescence from dilute rigid solutions of poly(2-vinylnaphthalene) serving as a probe in films of polystyrene has been used to monitor relaxation processes in the region of the glass transition temperature of the host polymer.[5] A further, very recent, application of the excimer fluorescence probe technique has appeared in which excimer fluorescence from poly(2-vinylnaphthalene) was utilized to probe compatibility in polymer blends.[6] This technique shows promise of being a useful method for studying polymer blend compatibility and, in particular, may allow one to extend compatibility studies into composition regions not accessible by the more classical methods. Morawetz has also addressed the problem of polymer blend compatibility through the use of luminescence measurements.[7] This method, in which the efficiency of nonradiative energy transfer between two polymers, one tagged with an energy donor and the other with an energy acceptor, is measured, appears to be a particularly powerful one since it is applicable to nonaromatic pendant group polymers devoid of excimer fluorescence.

Here the results of an investigation concerning the emission properties of poly(*N*-vinylcarbazole) (PVK) in solid films of polystyrene and poly(methyl methacrylate) are reported. The emission spectra of PVK in dilute blends of both host polymers are found to be dependent on the nature of the host polymer and the molecular weight of the PVK guest. These properties are shown to be related to the degree of compatibility between the guest and host polymers as reflected in the PVK guest chain dimensions and to the extent of energy migration along isolated PVK chains or phase-separated microdomains to preformed excimer-forming sites.

Experimental Section

Materials. Solutes. Narrow molecular weight fractions of PVK spanning a number-average molecular weight range of $2400 \leq \bar{M}_n \leq 500\,000$ were obtained from various research groups within these laboratories. The various molecular weight fractions were all obtained by fractional precipitation from benzene solution using methanol. In the high molecular weight region, the starting polymer was commercially available BASF Luvican M170 PVK. The starting polymers in the intermediate and low molecular weight regions were in-house synthesized materials. Details concerning the synthetic procedure can be found in a report by Griffiths and VanLaeken.[8] The weight-average molecular weight and number-average molecular weight were determined by gel permeation chromatography. It is important to note that all the PVK fractions investigated were synthesized by free radical initiation since it is known that cationically polymerized PVK has

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Table I
Weight-Average Molecular Weight, Number-Average Molecular Weight, and Molecular Weight Distributions of the PVK Fractions Investigated

$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
	2 400	
4 500	3 500	1.28
7 600	5 550	1.37
10 600	7 250	1.46
13 300	9 570	1.39
15 200	10 200	1.49
31 900	19 800	1.61
36 000	23 500	1.53
92 800	53 400	1.74
110 000	73 000	1.51
145 000	83 800	1.73
470 000	309 000	1.52[a]
667 000	343 000	1.95
600 000	500 000	1.20

[a] $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ values were not available for this fraction. The value of $\overline{M}_n$ tabulated was calculated by assuming the value of $\overline{M}_w/\overline{M}_n$ to be the average of the experimentally determined molecular weight distributions for all the other fractions.

a higher isotactic content than free radically polymerized PVK, which results in differences in the emission spectra of the two materials.[9] The various PVK fractions investigated are listed in Table I.

The various molecular weight fractions of polystyrene were all special standards obtained from Pressure Chemical Co. The poly(methyl methacrylate) was a bead polymer with an intrinsic viscosity of 0.4 dL/g supplied by Polysciences, Inc.

Solvents. Benzene (Burdick and Jackson Laboratories, Inc., distilled-in-glass grade) was used for preparing solutions for emission spectroscopy and for casting the majority of the polymer blend films. This was used as received. In some instances analytical reagent grade benzene from Mallinckrodt or toluene (Burdick and Jackson, distilled-in-glass grade) was used to prepare the solutions for film casting. These solvents were also used as received. The emission spectra of the resulting films were not dependent on which of the above solvents was used. Attempts to cast films with tetrahydrofuran as solvent generally yielded poor-quality films. These were not investigated.

Film Preparation. Films of the polymer blends were prepared by solvent casting from approximately 10 wt % solutions of solid polymer dissolved in benzene. Typically 100 mg of polystyrene (PS) or poly(methyl methacrylate) (PMMA) was weighed out on a microbalance and placed in a small glass vial. To prepare very dilute blends containing 0.25 wt % or less of PVK, the PS or PMMA was dissolved in 1 mL of a PVK–benzene solution of the appropriate concentration. In the case of blends containing higher weight percent PVK, the required amount of PVK was also weighed out on the microbalance, added to the vial containing the PS or PMMA, and dissolved in 1 mL of benzene. Films were cast by placing part of the prepared solution onto carefully cleaned $^1/_8$ in. × 1.25 in. fused-quartz disks. The quartz disks were covered and the solvent allowed to slowly evaporate at room temperature. The resulting films were typically about 20 μm thick. The films were then placed in a small oven and heated at ~55 °C for periods of time ranging from several hours to several days. The emission spectrum of a film measured immediately following the room-temperature evaporation was indistinguishable from the emission spectrum measured following days of storage at 55 °C.

In one instance, a series of films of constant composition but with varying PVK $\overline{M}_n$ was prepared in the following manner. The polymer solutions were purged with nitrogen gas to remove dissolved oxygen. The films were then cast in a glovebox in an inert atmosphere of argon. Following room-temperature evaporation of solvent in the argon atmosphere, the films were further dried at 55 °C in a nitrogen atmosphere. The emission spectra of these films were found to be virtually identical with those films in which no efforts were made to eliminate oxygen.

Films were also prepared at various casting temperatures. In these cases the vial containing the polymer solution, the quartz disk, and the transfer pipet were all placed in an oven and stored until the solution and glassware had achieved constant temperature. A small amount of solution was then quickly transferred from the vial and placed on the quartz disk. Solvent evaporation and film drying then proceeded at constant elevated temperature.

Fluorescence Measurements. Fluorescence spectra of the films were measured with a Perkin-Elmer Model MPF-44 fluorescence spectrophotometer. The films were mounted in the sample compartment at approximately 45° to the incident exciting light and back-illuminated such that reflected excitation and stray light was directed away from the entrance slit of the viewing monochromator. Detection was at 90° to the excitation. Fluorescence decay measurements were made by using the method of time-correlated single photon counting.[10] The electronics required for the nanosecond fluorescence decay apparatus were all obtained from Ortec, Inc., while the sample compartment was of our own design. Details concerning this instrument can be found in an earlier publication.[11]

Results and Discussion

Prior to presenting the results of the fluorescence measurements on the various polymer blends, it is of interest to review briefly the complex photophysical properties of PVK as observed in dilute fluid solution. The emission properties of PVK are unique among vinyl polymers containing aromatic pendant groups, including, in fact, other more open structured vinylcarbazole polymers such as poly(*N*-ethyl-2-vinylcarbazole), poly(*N*-ethyl-3-vinylcarbazole), and poly(*N*-ethyl-4-vinylcarbazole).[12] In general, vinyl aromatic polymers exhibit two types of fluorescence emission in dilute fluid solution; one is monomer-like fluorescence characteristic of the aromatic pendant group while the second is a structureless excimer fluorescence band occurring at lower energies. The intrachain excimer fluorescence results from the existence of local conformational states of polymer dyads in which two adjacent pendant groups achieve an eclipsed sandwich-like geometry with an intermolecular distance of 3.0–3.5 Å. Generally, the same excimer fluorescence will be observed as a result of intramolecular interactions of nonadjacent pendant groups if the large-scale conformation of the polymer is one in which the chain folds back on itself. The uniqueness of PVK lies in the fact that its emission spectrum is broad and structureless and does not exhibit the structured fluorescence band characteristic of an isolated carbazole moiety. Typical fluorescence spectra of PVK are shown in Figure 1 and 2.

The broad, structureless emission spectrum of PVK has, with the aid of fluorescence decay measurements and measurements of time-resolved fluorescence spectra, been resolved into two bands, one peaking near 420 nm and the other near 370 nm.[13,14] On the basis of studies with carbazole "double-molecule" model compounds, the band peaking near 420 nm has been assigned unequivocally as fluorescence from an excimer in which two carbazole groups have achieved an eclipsed, sandwich-like conformation.[11,15] The exact nature of the state responsible for the excimer-like fluorescence at 370 nm is not as well understood. It has been suggested that perhaps this fluorescence band arises from the interaction of two carbazole pendant groups, one electronically excited, the other in its ground state, in which there is significant deviation from the sandwich-like geometry or that there is only partial overlap of the two groups.[9,13] Following Klöpffer, we designate the 420-nm band "true excimer" fluorescence and the 370-nm band "trap II" fluorescence.[16]

Steady-State Fluorescence Measurements

Figure 1 displays the emission spectra of three different molecular weight fractions of PVK in PMMA blends along with the emission spectrum of one of these fractions in a

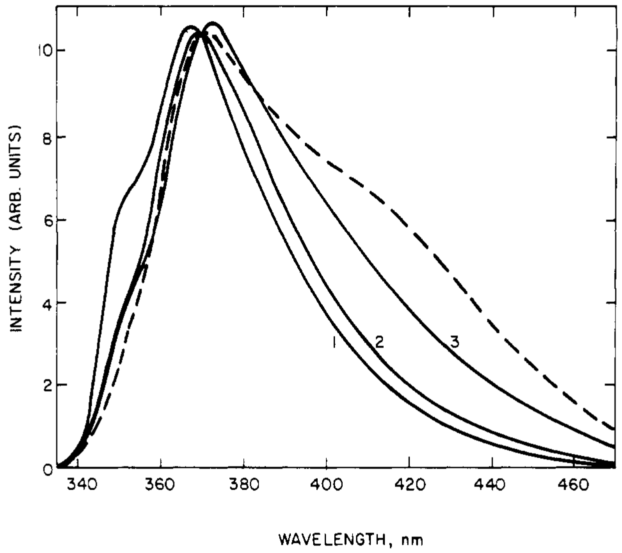

Figure 1. Typical emission spectra of 0.05 wt % poly(*N*-vinylcarbazole) of various number-average molecular weights in poly(methyl methacrylate) films (—) and in 10^{-4} M benzene solutions (---) at room temperature. (1) $\bar{M}_n = 5550$; (2) $\bar{M}_n = 23500$; (3) $\bar{M}_n = 83800$; (---) $\bar{M}_n = 23500$.

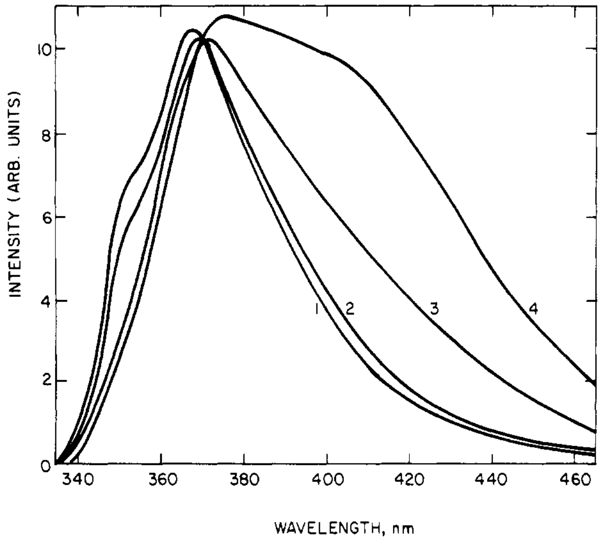

Figure 2. Typical emission spectra of 0.05 wt % poly(*N*-vinylcarbazole) of various number-average molecular weights in polystyrene films at room temperature. (1) $\bar{M}_n = 5550$; (2) $\bar{M}_n = 7250$; (3) $\bar{M}_n = 19800$; (4) $\bar{M}_n = 83800$.

dilute (10^{-4} M) fluid solution of benzene which had been purged with nitrogen to remove dissolved oxygen. The spectra shown in Figure 1 have been normalized to equal intensity at 370 nm. Two principal features are noted: first the true excimer fluorescence intensity relative to the trap II fluorescence intensity is observed to increase with increasing $\bar{M}_n$ in the polymer blends, and second the intensity of true excimer fluorescence relative to the trap II intensity observed in fluid benzene is considerably greater than that observed for the same molecular weight fraction of PVK in the solid polymer blend.

Figure 2 shows typical fluorescence spectra of four molecular weight fractions of PVK in blends of PS. Again, the molecular weight dependence of the PVK emission spectra is clearly evident and, in addition, it should be noted that the true excimer to trap II fluorescence intensity ratios observed in PS are greater than those observed in PMMA at equivalent values of $\bar{M}_n$. This particularly evident for the higher molecular weight fractions. These two observations, namely, the sensitivity of the true excimer to trap II fluorescence intensity ratios on the nature of the host polymer and the molecular weight dependence of this ratio, constitute the major findings of this investigation, and these will be considered in detail below.

The difference between the true excimer to trap II fluorescence intensity ratios (I_{425}/I_{370}) in fluid solution and solid film at the same PVK $\bar{M}_n$ can be understood through consideration of the excimer site concentration and the process by which these sites are populated. In dilute fluid solution it has been shown that there is a rapid interconversion of intrachain conformational states due to solvent collisions.[17] Consequently, excitation of these excimer sites can occur through a number of different mechanisms. If, for example, as is often the case, there is rapid migration of the initial electronic excitation along the polymer chain, then the excimer site can be populated by arrival of the excitation at a site in which two pendant group chromophores have achieved the eclipsed sandwich-like geometry necessary for true excimer fluorescence prior to the initial excitation. If, on the other hand, the initial excitation is localized on a pendant group during the time that the required geometry is achieved as a result of dynamic main-chain conformational changes, or side-group motions, excimer fluorescence will also occur. In the solid state this latter process, of course, cannot occur since main-chain conformational changes are frozen out or at least severely limited. Thus, in the polymer blends, the fluorescence results reflect the density of preformed excimer sites as determined by the equilibrium conformation of the PVK chains at the temperature at which the films were cast and the efficiency with which these sites are populated. The later factor depends on energy migration along the polymer chain—a process known to be very effective in the case of PVK.[18]

In fluid solution, at a temperature corresponding to that at which the polymer films were cast, the following conditions are expected to pertain if the thermodynamic differences between the solid polymer host and the fluid solution solvent are minimal. At any instant in time the main-chain equilibrium conformation in solution will be nearly the same as exists in the solid polymer blend and, thus, the density of preformed excimer sites which exist along a PVK chain, as determined by the chain conformational statistics, will be approximately the same in both phases. The rate of energy migration along the polymer chain should also be approximately equal in both cases since this is determined primarily by the high local concentration of pendant group chromophores. The contribution of true excimer fluorescence to the I_{425}/I_{370} ratio due to energy migration to preformed excimer sites should then be approximately the same in both fluid and rigid solution. In fluid solution rapid interconversion of main-chain conformational states yields, in essence, a higher density of true excimer sites since there now exists a kinetic pathway for their formation during the lifetime of a singlet excitation on the polymer chain.[17] Consequently, the intensity due to true excimer fluorescence will be greater, leading to a greater I_{425}/I_{370} fluorescence ratio.

Figure 3 presents the results of steady-state fluorescence measurements on a series of very dilute (0.05 wt %) blends of PVK in PS (MW = 50 000) as a function of the PVK number-average molecular weight. The ratio of the fluorescence intensity at 425 nm (I_{425}) to that at 370 nm (I_{370}) is plotted vs. the $\bar{M}_n$ of the PVK. These wavelengths were selected to represent the intensity due to the true excimer fluorescence and trap II fluorescence, respectively, since previous investigations concerning the emission properties of PVK have shown that at these wavelengths

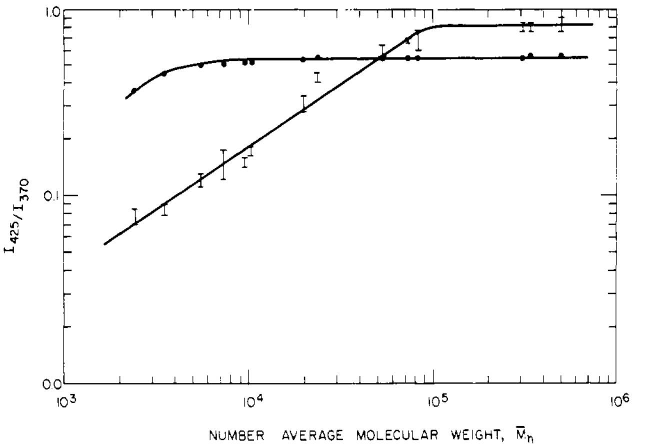

Figure 3. Ratio of the true excimer (I_{425}) to trap II (I_{370}) fluorescence intensities of poly(*N*-vinylcarbazole) in fluid benzene (●) and polystyrene (MW = 50 000) films (I) as a function of the number-average molecular weight of poly(*N*-vinylcarbazole).

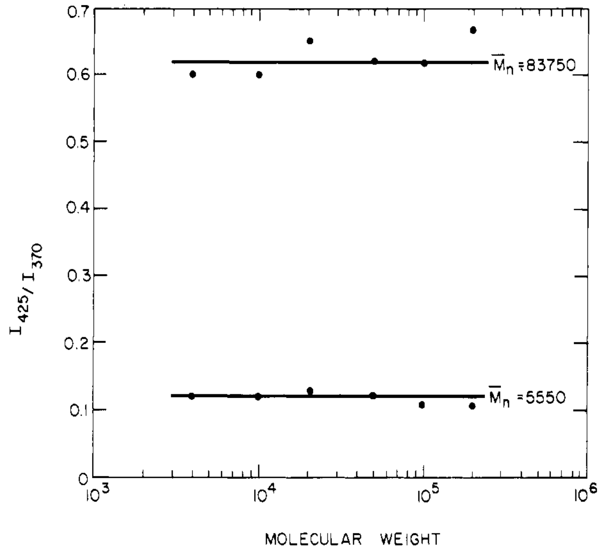

Figure 4. Ratio of the true excimer (I_{425}) to trap II (I_{370}) fluorescence intensities of poly(*N*-vinylcarbazole) in 0.05 wt % poly(*N*-vinylcarbazole)–polystyrene blends vs. the polystyrene molecular weight.

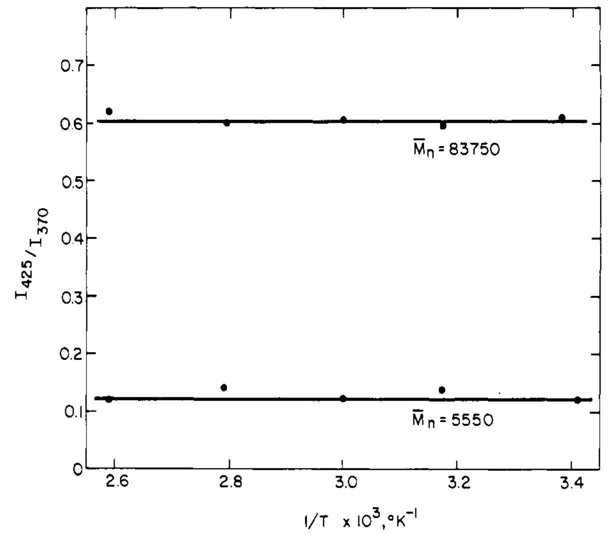

Figure 5. Ratio of the true excimer (I_{425}) to trap II (I_{370}) fluorescence intensities of poly(*N*-vinylcarbazole) in 0.1 wt % poly(*N*-vinylcarbazole)–polystyrene (MW = 50 000) blends vs. the film casting temperature.

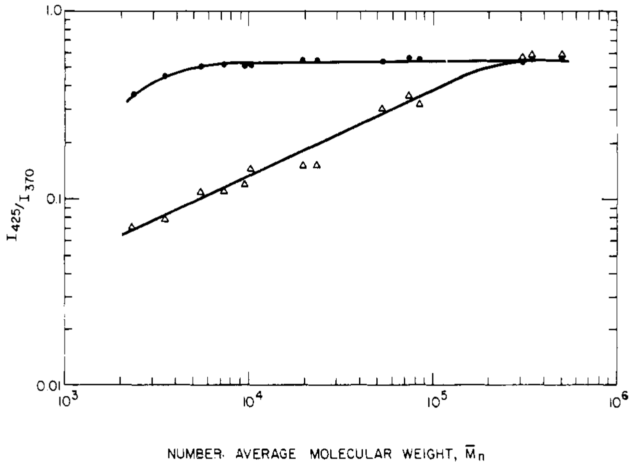

Figure 6. Ratio of the true excimer (I_{425}) to trap II (I_{370}) fluorescence intensities of poly(*N*-vinylcarbazole) in fluid benzene (●) and poly(methyl methacrylate) films (△) as a function of the number-average molecular weight of poly(*N*-vinylcarbazole).

the spectra are not unduly complicated as a result of the overlapping of the two types of emission. The I_{425}/I_{370} ratio is seen to increase with an increase in $\bar{M}_n$ of the PVK until at $\bar{M}_n \simeq 100\,000$ I_{425}/I_{370} achieves its maximum value and remains constant at higher $\bar{M}_n$ fractions. Over the range of $\bar{M}_n$ values spanning $2400 \leq \bar{M}_n \lesssim 100\,000$ the I_{425}/I_{370} ratio is proportional to the 0.67 ± 0.05 power of $\bar{M}_n$. It should be noted that the brackets spanning each I_{425}/I_{370} value, at a given value of $\bar{M}_n$, cover the results obtained on four different films, each cast or treated in a somewhat different fashion. These different film fabrication procedures have been noted in the Experimental Section. Clearly, the results obtained are not particularly sensitive to the method of film preparation. This insensitivity removes from concern potential complications associated with plasticization of the films due to solvent retention and the effect of oxygen, which is an effective quencher of carbazole fluorescence. The films share in common the fact that they were all cast and the spectra measured at room temperature and, hence, it is believed that we are probing at least near-equilibrium properties of PVK in the host polymers.[19] Identical results were obtained for 0.05 wt % PVK PS blends in which the PS molecular weight was 97 200 and 200 000. Figure 4 and 5 show typical results obtained on 0.05 wt % PVK blends in PS where the molecular weight of the PS is varied and for 0.1 wt % PVK blends in PS in which the film casting temperature was varied. The I_{425}/I_{370} ratios are not sensitive to these two experimental parameters. Figure 3 also contains the I_{425}/I_{370} ratios determined for 10^{-4} M solutions of PVK in benzene. Each solution was purged with nitrogen to remove dissolved oxygen immediately prior to the measuring of its emission spectrum. In dilute fluid solution, this ratio is seen to be independent of the PVK $\bar{M}_n$ except for the two lowest $\bar{M}_n$ fractions, for which there is some drop-off in this ratio.

Figure 6 presents the results obtained from the emission spectra of dilute (0.05 wt %) PVK in PMMA. The results are similar in nature to those observed in PS; however, there are some essential differences. First, the I_{425}/I_{370} ratio is proportional to the 0.45 ± 0.05 power of $\bar{M}_n$ as opposed to the value of 0.67 ± 0.05 observed in PS, and this power law behavior appears to extend to a $\bar{M}_n$ value of approximately 200 000 before saturation occurs as opposed to only approximately 100 000 in PS. The I_{425}/I_{370} ratios observed in PMMA are consistently less than those observed in PS at the same $\bar{M}_n$ of the PVK. In the low-$\bar{M}_n$ region, this difference is quite small but the difference increases with increasing $\bar{M}_n$. In the saturation region, the I_{425}/I_{370} values observed in PS are higher than those observed in fluid benzene, whereas in PMMA the value of I_{425}/I_{370} is about the same as the nearly $\bar{M}_n$-independent values observed in benzene solution.

Basically, two principal findings have emerged here. One is the variation in the I_{425}/I_{370} ratio in the two different host polymers at the same $\bar{M}_n$ value of PVK; the other is the different molecular weight dependence observed in each of the two hosts. The first effect apparently reflects differences in compatibility between the guest and host polymers and is not unexpected based on the work of Frank, who demonstrated that excimer fluorescence can serve as a molecular probe of polymer blend compatibility.[6] It is also well-known that blend compatibility depends on the molecular weight of the blend components. Thus, it is appropriate to ask whether the observed molecular weight dependence of the fluorescence ratios is a reflection of the expected decrease in blend compatibility with increasing probe molecular weight and whether the two different power law dependences of the ratios on $\bar{M}_n$ reflect in a more subtle manner differences in the degree of compatibility with the two host polymers. To address these questions, it is useful to recall the nature of excimer-forming sites in polymers and the fluorescence behavior of an excimer probe in a polymer blend as the blend components proceed from a condition of miscibility to immiscibility. Frank has discussed this in a particularly lucid fashion in which excimer-forming sites are classified into three types.[6] The first type results from the intermolecular interaction of pendant groups on different polymer chains and is important in concentrated solutions, in neat polymer films, and in blends in which phase separation occurs. The second types results from the intramolecular interaction of pendant groups on nonadjacent chain segments and can be important in those cases where the large scale chain conformation is such that chain folding is important. The third class results from the intramolecular interaction of pendant groups on adjacent chain segments. This class is important in all cases but particularly so in very dilute solutions or blends in which interchain interactions are absent. In solid films of dilute blends the excimer fluorescence intensity provides a measure of the density of g^-t and tg^- dyads in syndiotactic sequences and tt dyads in isotactic sequences which are populated by competitive trapping of migrating excitation.

Based on this classification of excimer sites in polymers, it is possible to speculate as to what might be expected to occur when an aromatic vinyl polymer is utilized to probe compatibility with a second polymer in a solid blend. By analogy with fluid solutions, one can consider an excimer probe polymer in a compatible host polymer as being in a good solvent while that in an incompatible polymer as being in a poor solvent. With the increase in chain expansion that occurs in increasingly good solvents, there is a corresponding decrease in the local concentration of pendant groups and, thus, one would expect a decrease in the excimer to monomer fluorescence ratio due to a decrease in the excimer site concentration, whereas in a poor solvent just the opposite would occur as a result of chain contraction. Frank observed an excellent correlation between the excimer to monomer fluorescence ratios of poly(2-vinylnaphthalene) serving as a probe in blends of poly(alkyl methacrylates) as hosts with the difference in solubility parameters of the probe and host polymers; the ratio was a minimum when the solubility parameters were approximately equal and the value of the ratios increased with increasing difference in solubility parameter.[6]

On the basis of this description alone, it would be concluded that PVK is less compatible with PS than with PMMA since the values of I_{425}/I_{370} are less for PVK in PMMA than in PS at all values of $\bar{M}_n$. However, here it is important to recall that the emission properties of PVK are unique; monomer fluorescence is not observed but instead a structureless, excimer-like band is seen in the 370-nm spectral region. Consequently, it does not necessarily follow that larger values of I_{425}/I_{370} imply a lesser degree of compatibility. A consideration of the PVK chain itself and its known photophysical properties leads to a rather simple, qualitative explanation of why the fluorescence ratios observed in PS and PMMA are, in fact, what should be expected in going from a more compatible to a less compatible system. As stated earlier, the low-energy emission band at 425-nm results from an excimer site in which two carbazole pendant groups achieve an eclipsed sandwich-like geometry whereas the 370-nm emission results from sites in which this fully eclipsed geometry is not achieved. In PVK, of course, the carbazole group is bonded to the chain backbone at the nitrogen atom. This is most significant since with this bonding arrangement it is not possible, except perhaps under the most unlikely set of interaction conditions, to achieve an increase in density of true excimer sites along a single polymer chain due to intramolecular interactions of nonadjacent pendant groups as a result of large-scale conformational changes such as chain contraction or back-bending. That is, it is not possible to achieve a coplanar sandwich-like conformation in which the two nitrogen atoms are apposed. Overlapping sandwich-like conformations in which the two nitrogens are not apposed are easily achieved but these are not true excimer sites. This will be true also when interchain interactions are important as in the case of neat films or in phase-separated domains of polymer blends. In PVK the true excimer site can only be formed between two nearest-neighbor pendant groups of the same polymer chain. Thus, even in films of neat PVK or in phase-separated domains in blends, the density of true excimer sites does not increase as a result of these interchain interactions in spite of the greatly increased local concentration of carbazole groups which exist under these conditions. The density of trap II sites, on the other hand, can increase as a result of this increased local concentration since these sites apparently result from intermolecular interactions in which the strict geometrical requirements necessary for true excimer fluorescence are not required. With this description of PVK and the previous discussion of excimer site sampling in mind, it follows that measurements of the ratio of true excimer to trap II fluorescence are expected to decrease with increasing incompatibility or with long-range conformational changes such as chain back-bending, contrary to what is expected in the case of an excimer probe polymer in which excimer to *monomer* fluorescence ratios is measured and the density of excimer sites increases with increasing incompatibility. From this it is concluded that the greater I_{425}/I_{370} ratio observed in PS than in PMMA for the same number-average molecular weight fraction of PVK indicates that PVK is more compatible with PS than with PMMA or that PVK experiences chain expansion in PS.

Support for the conclusion of greater PVK compatibility with PS than with PMMA, derived from the excimer fluorescence probe results, follows from consideration of observations based on the familiar criterion of optical clarity. The optical clarity of a number of PVK/PS and PVK/PMMA films containing different $\bar{M}_n$ fractions of PVK, and at different weight percent loadings, are listed

Table II
Optical Appearance of PVK-PS and PVK-PMMA Blends Containing Different Number-Average Molecular Weight Fractions and Weight Percent Loadings of PVK

PVK $\bar{M}_n$	optical clarity: PS-0.05 wt % PVK	PMMA-0.05 wt % PVK	PMMA-0.5 wt % PVK
2 400	clear	clear	clear
3 500	clear	clear	clear
5 500	clear	clear	clear
7 250	clear	clear	clear
9 570	clear	clear	clear
10 200	clear	clear	hazy
19 800	clear	clear	hazy
23 500	clear	clear	hazy
53 400	clear	clear	hazy
73 000	clear	clear	hazy
83 800	clear	clear	hazy
309 000	clear	hazy	hazy
343 000	clear	hazy	hazy
500 000	clear	hazy	hazy

PVK, wt %	optical clarity: PS-PVK $\bar{M}_n$ = 83 800	PMMA-PVK $\bar{M}_n$ = 83 800
0.01	clear	clear
0.025	clear	clear
0.05	clear	clear
0.1	clear	hazy
0.25	clear	hazy
0.5	hazy	hazy
1	hazy	opaque
2	hazy	opaque
3		opaque

in Table II. The appearance of haziness or opacity indicates unequivocally that phase separation has occurred while optical clarity can indicate a number of different possibilities. Optically clear films will result if the blend components are miscible. However, optical clarity will also occur in immiscible systems in those cases where the refractive indices of the components match or if the domain size is small with respect to optical wavelengths. The refractive indices of PVK, PS, and PMMA are 1.68, 1.58–1.60, and 1.486–1.490, respectively; hence each is sufficiently different to eliminate the possibility of masking phase separation due to index matching.[20] The optical appearances of a number of different films are listed in Table II. The results appear to be in general accord with the Flory–Huggins–Scott theory in that compatibility decreases with increasing molecular weight of the PVK. Furthermore, it is noted that phase separation is visibly evident at a lower weight percent PVK in PMMA than in PS, indicating that PVK exhibits a higher degree of compatibility with PS than with PMMA.

A final point of concern relates to the results shown in Figures 3 and 6, in which the I_{425}/I_{370} ratio is plotted vs. the PVK $\bar{M}_n$. These results were obtained on very dilute blends which typically were optically clear. At these very low concentrations of the probe polymer, it is not clear then whether one is measuring the properties of a system in which phase separation has occurred but the domain size is too small to yield visually detectable light scattering or whether the probe polymer exists as molecularly dispersed individual chains. This is a dilemma that arises in any discussion of polymer blend compatibility and, as noted by Krause in her comprehensive review of blend compatibility, there always exist compositions above a lower critical solution temperature or below an upper critical solution temperature where complete miscibility exists if one of the blend components is sufficiently dilute.[21] To address the question as to what happens when phase separation is visibly evident, the fluorescence spectra of a number of films containing different weight percentages of PVK were measured. Figure 7 and 8 show the results of I_{425}/I_{370} measurements as a function of the PVK weight percent in PS and PMMA, respectively. The I_{425}/I_{370} ratio is seen to be relatively insensitive to the PVK concentration in both host polymers. There is a gradual increase in this ratio as the PVK concentration increases, but there is no discontinuity in the curves at those compositions where optical evidence of phase separation was observed. The ratios, in fact, seem to remain constant and then slowly increase monotonically toward a value of 1.4 ± 0.1, which was observed from films of neat PVK of various molecular weights. On the basis of this, it is felt that at the rather low weight percent loadings used to gather the data of Figures 3 and 6, the results reflect properties of isolated PVK chains rather than microdomains although it is not possible to reject this possibility outright.

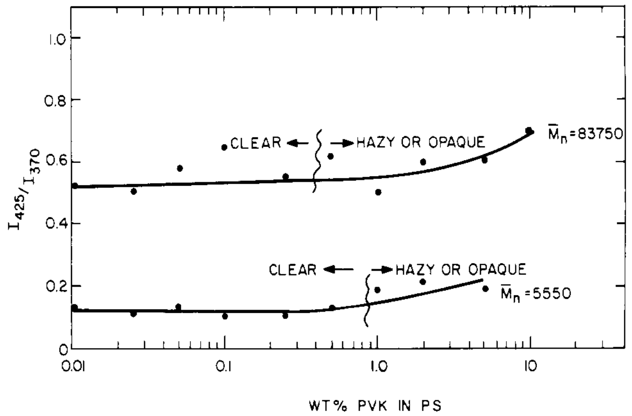

Figure 7. Ratio of the true excimer (I_{425}) to trap II (I_{370}) fluorescence intensities of poly(*N*-vinylcarbazole) in polystyrene vs. the weight percent of poly(*N*-vinylcarbazole).

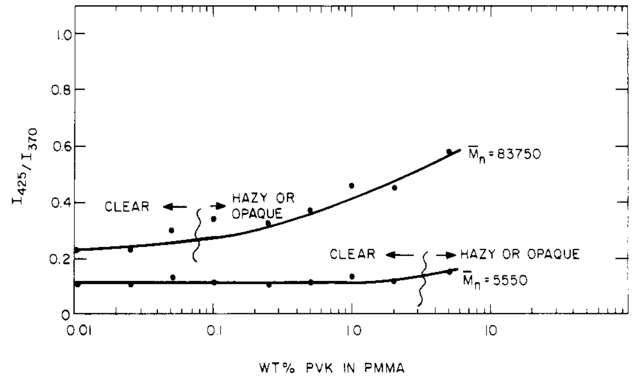

Figure 8. Ratio of the true excimer (I_{425}) to trap II (I_{370}) fluorescence intensities of poly(*N*-vinylcarbazole) in poly(methyl methacrylate) blends vs. the weight percent of poly(*N*-vinylcarbazole).

At this point it might be useful to compare the properties of PVK in PS blends with those observed by Frank and co-workers for poly(2-vinylnaphthalene) in PS and to point out the rather striking differences between the behavior of these two excimer probes. In the case of PVK, as shown in Figures 4, 5, and 7, the I_{425}/I_{370} ratios are independent of (1) the molecular weight of the PS host, (2) the temperature at which the films were cast, and (3) the weight percent of the PVK contained in the blend. Each of these findings is contrary to the behavior of poly(2-vinylnaphthalene) in PS, where the excimer to monomer fluorescence ratio was found to be sensitive to all of the above experimental variables.[6] This suggests that the relationship between the intramolecular interactions which occur in isolated polymer chains as a result of their conformational properties and the intermolecular interactions which occur within phase-separated domains with measured photophysical properties is highly specific for different probes and, thus, it will not be possible to formulate any generalizations regarding the utility of excimer fluorescence as a probe for polymer blend compatibility. A particularly disappointing feature of the PVK results is the small change in the I_{425}/I_{370} ratio with increasing weight percent of the PVK, even at those loadings where phase separation has clearly occurred as evidenced by the appearance of optical turbidity and the independence of this ratio on the molecular weight of the PS host. In contrast, one of the primary attributes of poly(2-vinylnaphthalene) as a probe for blend compatibility is the sensitivity of the excimer to monomer fluorescence ratio to both the concentration of the guest polymer and the molecular weight of the host. It was this variation which enabled the excimer probe method to assist in the generation of the thermodynamic phase diagram for the blend by extending it to compositions where phase separation had occurred, as evidenced by the fluorescence ratios, but where the domain size is below the limits of visual detection. In this sense, PVK must be regarded as a rather poor probe since it does not display utility in the determination of a phase diagram for these blends. The different I_{425}/I_{370} ratios observed in PS and PMMA can be used only in a gross manner to imply greater compatibility of PVK and PS than with PMMA while the different molecular weight dependences observed in the two hosts can be related to the PVK guest chain dimensions in a manner which we think can be understood by analogy with the thermodynamics of polymer solutions.

The molecular weight dependence of the excimer to trap II fluorescence ratios observed in both PS and PMMA (Figure 3 and 6) is clearly indicative of the existence of preformed excimer sites which are populated by a process involving migration of the initial excitation along the polymer chain. The change in the excimer to trap II fluorescence intensity ratios was found to follow the expression

$$I_{425}/I_{370} = K\bar{M}_n^{\alpha} \tag{1}$$

where $\alpha = 0.67 \pm 0.05$ for PS and $\alpha = 0.45 \pm 0.05$ for PMMA over the molecular weight range $2400 \leq \bar{M}_n \lesssim 100\,000$ for PS and $2400 \leq \bar{M}_n \lesssim 200\,000$ for PMMA. The I_{425}/I_{370} ratios are constant at all higher $\bar{M}_n$ fractions of PVK in the respective host polymers. This saturation behavior is also consistent with the existence of preformed excimer sites which are populated by trapping of the initial excitation which migrate along a chain or within a microdomain. For PVK fractions with $\bar{M}_n \gtrsim 100\,000$ in PS and $\bar{M}_n \gtrsim 200\,000$ in PMMA, the polymer chain conformational statistics are such that there is at least one true excimer site within a diffusion length of the initial excitation for essentially every PVK chain. The expression for the molecular weight dependence of the fluorescence ratios is seen to be of the same form as the familiar Mark–Houwink equation which relates the variation of intrinsic viscosity with molecular weight. In the Mark–Houwink equation, the value of the exponent (equivalent to the α of eq 1) is a measure of the chain dimensions. These exponents are typically found to vary between 0.5 and 0.8, with the value of 0.5 being observed under Θ conditions and the higher values characteristic of good solvents, and the correspondingly greater chain expansion which occurs therein. It seems reasonable then to interpret the value of the exponent α in eq 1 as reflecting in some manner the PVK chain dimensions in PS and PMMA. With this interpretation of α the values obtained for PS and PMMA are consistent with the earlier conclusions based on optical appearance and fluorescence ratios that PVK exhibits a higher degree of compatibility with PS than with PMMA. This higher degree of compatibility is reflected in the greater chain expansion of PVK in PS while in PMMA it appears to have its unperturbed dimensions characteristic of a Θ solvent.

To conclude this section, it is necessary to comment about the above interpretation which relates the fluorescence ratios of the PVK guest polymer to its chain dimension in the respective host polymers. The fact that the molecular weight dependence of the excimer fluorescence ratios follows an expression of the same functional form as the Mark–Houwink expression relating intrinsic viscosity and molecular weight does not, of course, by itself, constitute proof that, in fact, the fluorescence ratios are also measures of the chain dimensions. The fluorescence ratios are, however, clearly a measure of the density of excimer states which exist along the polymer chain (or domain) and the density of these states are a function of the polymer chain configurational and conformational properties (or state of aggregation). It is, in fact, this property which forms the basis for the utilization of excimer fluorescence as a probe for polymer miscibility and leads to the often observed sensitivity of the fluorescence of certain excimer-forming polymers to the thermodynamic quality of the solvent in fluid solution. On the other hand, it will be recalled that earlier it was argued that in PVK the formation of true excimer sites can only occur between adjacent pendant groups, and excimer fluorescence from these sites is a measure of certain types of local conformational states, namely, tt conformations in isotactic chain sequences and tg^- or g^-t conformations in syndiotactic chain sequences. On this basis it might be argued that PVK should exhibit no sensitivity to solvent since it is generally held to be true that local conformational states of polymers are insensitive to solvent effects. However, there can be no question that since the large-scale conformation is solvent dependent, there must be some change in the density of certain local conformational states since it is the sum total of each local conformation that ultimately determines the polymer chain dimensions. It is of interest then to consider whether, in fact, the increased I_{425}/I_{370} ratios observed in PS compared to PMMA at the same PVK number-average molecular weight and the stronger molecular weight dependence in PS ($\alpha = 0.67 \pm 0.05$) than in PMMA ($\alpha = 0.45 \pm 0.05$), which have been interpreted as reflecting greater PVK chain expansion in PS than in PMMA, are consistent with certain other properties of PVK. We assume that in PMMA PVK acquires essentially its unperturbed dimensions characteristic of a Θ solvent. Under these conditions, the fluorescence ratios are a reflection of the density of true excimer sites and trap II sites which exist in the unperturbed or standard state of the PVK chains. The density of these states, as noted earlier, is dependent upon both the configurational and conformational aspects of the polymer chain. In this regard, it would be most useful if the two different excimer bands could be assigned to specific structural elements of the PVK chain such as, for example, the true excimer fluorescence to meso dyads and the trap II fluorescence to racemic dyads each in the appropriate conformation. The findings of Itaya et al. that cationically polymerized PVK has a higher isotactic content than free radically polymerized PVK and that the cationically prepared polymer exhibits more true excimer fluorescence

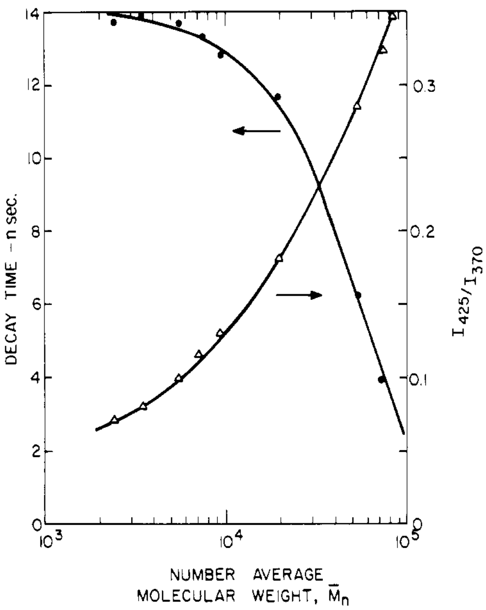

Figure 9. Comparison of the 370-nm fluorescence decay time and the true excimer (I_{425}) to trap II (I_{370}) fluorescence intensity ratios of poly(*N*-vinylcarbazole) in 0.05 wt % poly(*N*-vinylcarbazole)–poly(methyl methacrylate) blends.

relative to trap II fluorescence than does free radically prepared material suggest that perhaps the true excimer fluorescence band originates within those meso dyads which have or can achieve the proper tt conformation.[9] (In this regard see also ref 22.) Of course, true excimer fluorescence should also be observed from g$^-$t and tg$^-$ conformations of racemic dyads within syndiotactic chain sequences; however, the findings of Bokobza, Jasse, and Monnerie using polystyrene model compounds indicate that the meso dyad is more favorable for excimer formation than racemic dyads.[23] As noted earlier, the origin of the 370-nm or trap II fluorescence from PVK is presently still not totally understood although it is known that this state exists along the PVK chain prior to the initial excitation of a pendant group.[13] For purposes of this discussion, we speculate that it arises from the tt conformation of a racemic dyad since this a preferred ground-state conformation and with slight distortion allows for partial overlap of two adjacent carbazole pendant groups. Within this necessarily speculative and qualitative model, interpretation of the above results in terms of increased PVK chain expansion in PS is reasonable since an increased probability of having tt conformations of meso dyads along a chain should yield an increased density of true excimer-forming sites along with an increase in chain dimensions.[24] Even if the greater chain expansion also yields an increased density of tt conformations of racemic dyads, from which it is presumed the trap II fluorescence originates, the dominant effect on the I_{425}/I_{370} ratio must be due to the true excimer-forming site since this is the lowest energy state in the system.

Fluorescence Decay Measurements

Along with the previously discussed steady-state fluorescence measurements transient fluorescence decays were also measured on films of PVK in both PS and PMMA. Because of the very complex nature of the decay curves, only their most qualitative aspects will be presented and discussed here. In this regard, it should be noted that the most recent results on the fluorescence decay of PVK in solution, measured near 370-nm, have shown that the decay curve can be fitted to the sum of the three exponential functions.[25] The time required for the 370-nm intensity to decay to e^{-1} of its initial value is shown in Figure 9 as a function of the $\bar{M}_n$ of the PVK in a series of 0.05 wt % PVK–PMMA blends and compared to the values of I_{425}/I_{370} measured on the same film. Results obtained on 0.05 wt % PVK–PS blends were similar in nature. The purpose of Figure 9 is to simply show that the 370-nm fluorescence decay times, like the I_{425}/I_{370} ratios, are dependent upon the molecular weight of the PVK and vary in a fashion which is approximately the inverse of the variation of the I_{425}/I_{370} ratio with $\bar{M}_n$. Thus, as the value of I_{425}/I_{370} increases as a result of an increase in $\bar{M}_n$, the value of the 370-nm decay time decreases. It was further noted that $\tau_{370}(e^{-1})$ achieves a constant value at $\bar{M}_n \gtrsim 200\,000$, corresponding to the previously noted saturation of I_{425}/I_{370} ratios at these values of $\bar{M}_n$. The fluorescence decay times and the steady-state fluorescence results are thus both consistent with an interpretation in which the number of preformed true excimer sites per macromolecular chain increases with $\bar{M}_n$ and that at least one of the states contributing to the 370-nm intensity experiences a decrease in lifetime as a result of the increased probability of nonradiative deactivation due to migration and subsequent trapping at true excimer sites.

Synopsis

The emission properties of various molecular weight fractions of PVK serving as guests in films of PS and PMMA have been investigated. The fluorescence spectra of the various PVK fractions were found to be molecular weight dependent in films of the host polymers, and a different molecular weight dependence was observed for each host. Arguments based on the photophysical properties of PVK were presented to show that these effects are a consequence of differences in the PVK chain dimensions in the different hosts. The initial intent was to utilize the excimer fluorescence from PVK as a probe to determine its compatibility with PS and PMMA; however, it appears that PVK is not a particularly useful probe in this regard since it does not exhibit utility in elucidating the thermodynamic phase diagram of the blend system. By this it is meant that the emission properties of PVK are such that the results do not allow one to probe immiscibility at compositional regimes beyond those at which immiscibility is evident through light scattering. It is clear, however, that the results do reflect the influence of the host polymer (solvent) on the photophysical properties of PVK, and thus to the extent that the guest–host interaction ultimately determines the compatibility of the system, the results are a reflection of this property. It was determined that PVK experiences chain expansion in PS while in PMMA it has dimensions characteristic of its unperturbed state. On this basis, PVK is claimed to exhibit a higher degree of miscibility with PS than with PMMA.

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Molecular Weight Effects on Triplet Sensitization of Poly(2-vinylnaphthalene) in Benzene[†]

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ABSTRACT: The triplet state of poly(2-vinylnaphthalene) (P2VN) can be sensitized by a large number of molecules excited at 337.1 nm (N_2 laser), where P2VN has negligible absorption. It has been found that in benzene solution the sensitization rate (k_q) varies with the degree of polymerization according to the proportionalities $k_q \propto P^{-0.41}$ for exothermic sensitizers ($\Delta E_T > 3$ kcal mol^{-1}, where ΔE_T is the sensitizer–naphthalene energy gap) and $k_q \propto P^{-1}$ for $\Delta E_T < 3$ kcal mol^{-1}. The former dependency has been rationalized on the basis of the coil dimensions (radius of gyration) and the latter on the basis of residual unsaturation at the chain ends created by the chain termination during the polymerization reaction.

Introduction

We reported earlier that the quenching of the triplet state of poly(2-vinylnaphthalene) (P2VN) by piperylene displayed a pronounced molecular weight effect.[1] Likewise, there have been other reports of molecular weight and coil effects on small-molecule–polymer reactions in room-temperature solutions such as macroradical–scavenger reactions,[2] triplet-state sensitization, and quenching of polymers.[3–5] We have previously argued[1] that the bimolecular rate constant for a very efficient reaction of a small molecule with a side group of a homologous polymer should depend on the coil density according to the porportionality

$$k \propto [\eta]^{(a-2)/3a} \qquad (1)$$

where the variable a is the exponent in the Mark–Houwink relationship $[\eta] = KM^a$. However, the above proportionality is expected to hold only for very efficient reactions. As Winnik and Maharaj[6] have argued, if the reaction rate becomes slow, then all molecular weight effects should vanish. Our original aim in this study is to systematically examine the molecular weight effect on the bimolecular rate constant for P2VN when the small-molecule–polymer reaction becomes less efficient. Our experimental method is to study the triplet sensitization of P2VN with sensitizers that vary with respect to the energy of the lowest triplet state. The sensitization of P2VN was studied in preference to the quenching of the P2VN triplet because of the ambiguity that may result from the effect of triplet energy migration along the polymer of the bimolecular quenching rate constant.[1] As discussed in the Discussion, the triplet sensitization of P2VN with efficient sensitizers followed a proportionality like that of eq 1 but deviated from this relationship as the sensitization reaction became less efficient. The deviation is discussed in terms of a "two-state" model.

Experimental Section

Poly(2-vinylnaphthalene) was radically polymerized by outgassing a benzene solution (~20 wt %) of 2-vinylnaphthalene (twice vacuum sublimed) with a weight percent of azobis(isobutyronitrile) initiator from 0.04 to 0.64 for samples 1–3. The

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[†] This work was reported at the 28th Congress of the International Union of Pure and Applied Chemistry, Aug 16–22, 1981, Vancouver, B.C., Canada.

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