dinates to macroscopic control. While this criticism would be justified if the boundary junctions were elements of the system I, from the present viewpoint they belong to the system E and therefore must be described in macroscopic terms.
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Effect of Polystyrene Molecular Weight on the Fluorescence of Molecular Rotors

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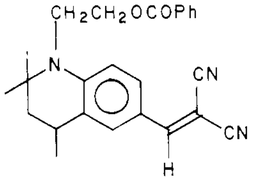
ABSTRACT: The effect of polystyrene molecular weight on the fluorescence intensity of a molecular rotor, [*p*-(dialkylamino)benzylidene]malononitrile derivative 1, has been studied. The fluorescence intensity of 1 increases gradually with the molecular weight of the host polymer up to a critical M_n of 10^4. This increase in fluorescence was attributed to a decrease in the polymer free volume. An abrupt rise in the fluorescence of 1 in PS with $M_n > 10^4$ was attributed to a change in the bulk morphology of PS due to polymer chain contraction or coiling as Θ conditions.

Polymer chain interpenetration has been extensively studied by luminescence spectroscopy.[1-8] Morawetz et al.[1] described the characterization of polymer compatibility by nonradiative energy transfer between suitably chosen fluorescence labels attached to the polymeric species. Another popular approach involves the use of excimer emission of polymers with aromatic side chains. In solutions of polystyrene, the ratio of excimer to monomer fluorescence intensity (I_e/I_m) increases with increasing polymer molecular weight[2,3] and concentration, since intermolecular chromophore interaction becomes increasingly important.[4] The molecular weight effect on I_e/I_m is not confined to polystyrene; dilute solutions of poly(1-naphthyl methacrylate,[5] poly(α-vinylnaphthalene),[6] and poly(2-vinylnaphthalene)[7] exhibit similar behaviors. Similar increases in I_e/I_m were observed with polymeric fluorescence probes such as poly(2-vinylnaphthalene)[8] or poly(vinylcarbazole)[9] dissolved in glassy films of nonfluorescent host polymers. This change is interpreted as signaling immiscible behavior on a small distance scale. As the host matrix becomes a thermodynamically poorer solvent for the guest probe, the extent of mutual interpenetration of the guest and host chains will decrease, causing the local concentration of the guest aromatic rings to rise and increasing the number of intermolecular excimer sites.

The versatility and sensitivity of luminescence as a technique to probe polymer chain interpenetration and polymer blend miscibility stem from the multiple aspects of the inter- and/or intramolecular interaction of electronically excited state with their immediate environment.[1-10]

This paper reports studies of the effect of the molecular weight of monodisperse atactic polystyrene as nonfluorescent host polymer on the fluorescence yield of a molecular rotor, [*p*-(dialkylamino)benzylidene]malononitrile 1.[11,12] This system was selected for several reasons.



Narrow-distribution polystyrene samples of different molecular weight are commercially available. The luminescence properties of polystyrene in solution as a function of molecular weight, concentration, and solvents have been studied.[2-4] In addition, polystyrene has been previously used as a host polymer for several polymeric fluorescent probes[7-9] but not for a molecular rotor probes. Finally, the glass transition temperatures of the polystyrene samples used are all above room temperature, making it possible to "freeze in" and study the chain conformation distribution when films are cast at room temperature.[13] The molecular rotor dyes used exhibit an exceptionally high rate of internal conversion, $\sim 10^{11}$ s^{-1}, attributed to torsional relaxation,[12] and this rate is media free-volume dependent. These dyes are therefore, excellent microscopic probes for measuring the torsional rigidity of the surrounding polymer, and the fluorescence yield is very sensitive to polymer structure and conformation.

The polystyrene samples were standards with narrow molecular weight distribution, ($M_w/M_n \leq 1.04$) from Pressure Chemical Co. Dye 1 was purified as described previously.[11] The spectroscopic measurements were made at relatively low dye concentration ($\leq 0.5\%$) to avoid dye aggregation or dimer formation. Films of dye 1 (0.5 wt %)

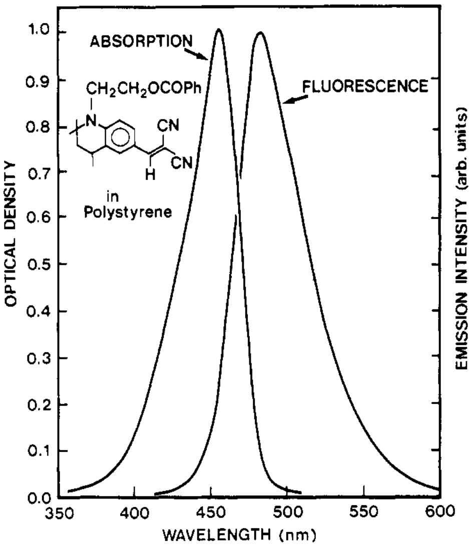


Figure 1. Absorption and fluorescence spectra of 1 in polystyrene film. The dye concentration was 0.05% by weight; film thickness was about 8 μm.

in atactic polystyrene (a-PS) of various molecular weight were prepared by solvent casting from 10% solution of polymer dissolved in spectrophotometric grade methylene chloride. Typically 100 mg of a-PS was dissolved in 1 mL of 0.05% 1 in methylene chloride. Films were cast by placing part of the prepared solution onto precleaned 2 in. × 2 in. Corning glass plates. The glass plates were covered and the solvent was allowed to slowly evaporate at room temperature. The resulting films were typically about 8 μm thick. The films were then placed in a small vacuum oven for 24 h. The emission spectrum of a film measured immediately following the room-temperature evaporation was not different from the emission spectrum measured following days of storage under vacuum. We also found no difference in the emission results after the samples were heated for a few hours above T_g.

The fluorescence spectra of the films were recorded at 23 °C by front-surface illumination on a Perkin-Elmer MPF-4 spectrofluorometer, which was equipped with a differential corrected spectral unit. Fluorescence quantum yield, Φ_f, was determined (in a corrected mode) by comparing with 9,10-diphenylanthracene fluorescence in poly(methyl methacrylate), which has been shown to have a Φ_f of 0.99.[14] The absorption spectra of dye 1 in a-PS films were measured on a Cary 17 spectrometer.

Typical absorption and fluorescence spectra of dye 1 in a-PS film are shown in Figure 1. The dye exhibits an intense absorption ($\epsilon_{max} = 5 \times 10^4$ M^{-1} cm^{-1}) at λ_{max} 450 nm and a weak fluorescence emission band at λ_{max} 485 nm. The widths of the absorption and emission bands were found to be the same in all PS films and independent of molecular weight. However, the quantum yield of fluorescence was very sensitive to the host polystyrene molecular weight. The fluorescence data of 1 in varying molecular weight of PS from 10^2 to 10^6, are given in Table I and plotted in Figure 2. The fluorescence yield of dye 1 increases gradually with the increase of polystyrene molecular weight up to $M_n = 10\,000$. Between $M_n = 10^4$ and M_n 10^5, ϕ_f increases rapidly by about a factor of 2 to a plateau that extends to $M_n = 1.8 \times 10^6$. This fluorescence behavior of the molecular probe is qualitatively very similar to that observed for poly(2-vinylnaphthalene) guest in PS solution.[8] However, the origin of the change in the fluorescence of the two probes with PS molecular weight must be different, since in our experiment a molecular rather than a polymeric probe was used. Probe miscibility with the host polymer is not an issue here.

Table I
Dye Fluorescence in Polystyrene with Varying Molecular Weight

polystyrene		dye fluorescence
M_n	T_g,[a] °C	$\Phi_f/10^{-3}$ [b]
1.04×10^2	−130	3.0
8.0×10^2	27	4.9
2.0×10^3	49	6.8
4.0×10^3	59	7.5
5.0×10^3	64	7.6
9.0×10^3	83	8.2
1.75×10^4	94	11.1
5.0×10^4	100	15.0
1.0×10^5	104	18.5
2.23×10^5	105	19.6
1.8×10^6	107	19.3

[a] See ref 16. [b] Measured at 23 °C; estimated error ±10%.

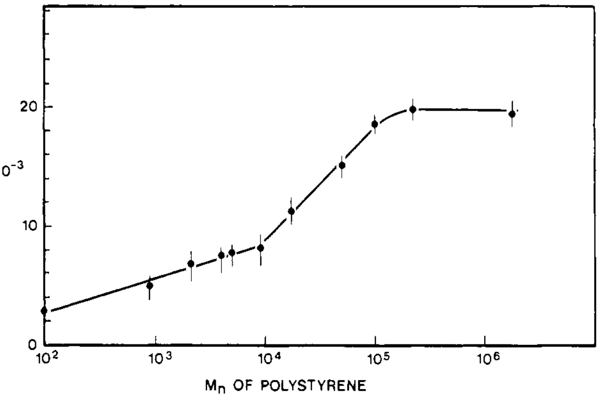


Figure 2. Variation of 1 fluorescence with polystyrene molecular weight, M_n.

The salient features of these results which we wish to explain are the initial gradual increase of guest fluorescence on host molecular weight to a critical M_n of 10^4 and the significance of the abrupt rise Φ_f for host molecular weight greater than 10^4. Before we present the morphological interpretation, we review briefly several aspects of the photophysics of the molecular rotors.

The $S_0 \rightarrow S_1$ transition of 1 was previously assigned to an intramolecular charge-transfer state.[11] The radiative rate constant, k_r, of the emitting singlet excited state of 1 is 2.28×10^8 s^{-1} (i.e., $\tau_r = 3.6$ ns), while the nonradiative decay rate, k_{nr}, is of the order of 10^{11} s^{-1}. Since these dyes exhibit very little triplet yields, the main pathway for nonradiative deactivation of the excited state is internal conversion. The absence of change in fluorescence emission maximum between room temperature and 77 K and the approach of Φ_f to unity at 77 K indicate that the emitting state must be those excited states that maintain a ground-state conformation. Previous work[11,12,15] has shown that for molecular rotors such as 1 torsional motion in the excited state is capable of inducing radiationless decay, $S_1 \rightarrow S_0$. It has also been suggested based on the substantial increases in the fluorescence yield in highly viscous solvent, polymers and frozen glasses that the torsional motion, responsible for inducing radiationless decay, is hindered by the viscous drag of the media. Rotation of the aryl group in the excited state is considered the rate-determining step, leading to rapid internal conversion to the ground state. In highly viscous solvents or in polymeric media,[12] we have shown that free-volume availability becomes the controlling factor in the torsional relaxation of the molecular rotors such as 1. Restricting the internal

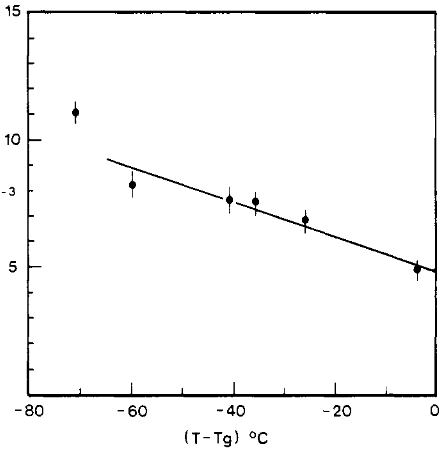


Figure 3. Dependence of 1 fluorescence on the glass temperature of the polystyrene matrix.

motion of the dye leads to a decrease in k_{nr} and consequently an increase in fluorescence.

On the basis of this description, the gradual increase in fluorescence efficiency of dye **1** with increase in the molecular weight of the host polystyrene to $M_n \leq 10^4$ can be attributed to inhibition of radiationless decay by rigidization of the probe by local environment. This arises entirely from a decrease in the available free volume as the molecular weight of PS increases. Since the change in the glass transition temperature, T_g, with M_n is due to changes in free volume, a correlation between Φ_f of **1** and T_g of the host polymer is expected. Figure 3 shows the variation of Φ_f of **1** with the T_g of PS.[16] The linear dependence of Φ_f on T_g observed here (for $M_n \leq 10^4$) supports the validity of the free-volume concepts as the controlling factor of torsional motion of the excited dye.

The situation is quite different for $M_n > 10^4$ and $M_n < 10^5$; the fluorescence of **1** abruptly increases by a factor of 2 and then levels off at $M_n > 10^5$. In that molecular weight range the glass transition temperatures of PS hardly changes. It should also be noted that all films prepared were optically clear; thus it might be argued that no phase separation has occurred.

The simplest possible explanation of the sudden rise in the fluorescence of the molecular probe **1** in PS above a critical molecular weight, $M_c \simeq 10^4$, is due to an abrupt change in the morphology of the bulk polymer resulting from chain contraction, coiling, or entanglement (a conformational state similar to the polymer in Θ solvent). Since the torsional motion of the probe becomes progressively restricted by chain contraction, this process effectively decreases the non-radiative decay rate, k_{nr}, of the probe, leading to the sudden rise in fluorescence above that critical M_n. At PS molecular weight greater than 10^5 a polymer network will form and at this point the fluorescence levels off. If this explanation is correct, for the first time we have a measure of the onset of the Θ condition in bulk solid films. It should be noted that neutron coherent scattering measurements on monodisperse polystyrene films of molecular weight ranging from 2×10^4 to 1.1×10^6 have shown that the conformation of PS molecules in the solid amorphous state is indistinguishable from that in Θ solvents.[17] Unfortunately, the conformation of PS molecules in an amorphous solid state of molecular weight $<2 \times 10^4$ is not available. Recent rheological tests have also shown that moderate molecular weight PS's in the melt and in concentrated solutions are a Θ solvent for the higher molecular weight fraction.[18]

The fluorescence data seem consistent with an expanded polymer chain for low molecular weight PS and contraction of the polymer chains as the molecular weight increases, reaching Θ conditions. However, alternative explanations such as polymer chain overlap or entanglement might also be possible.

The fluorescence of a molecular rotor, [*p*-(dialkylamino)benzylidene]malononitrile **1**, in solid films of monodisperse polystyrene increases gradually with the molecular weight of the host polymer up to a critical M_n of 10^4. This increase in the fluorescence was attributed to a decrease in the polymer matrix free volume which is available for the probe to rotate. A sudden rise in the fluorescence of **1** in PS with $M_n > 10^4$ was attributed to change in bulk PS morphology due to polymer chain contraction or coiling as in the Θ condition.

Registry No. Polystyrene, 9003-53-6; [[1-[2-(benzoyloxy)ethyl]-1,2,3,4-tetrahydro-2,4,6-trimethyl-6-quinolinyl]methylene]propanedinitrile, 74677-08-0.

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