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Intramolecular Energy Transfer, Migration, and Trapping in Polystyrene

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ABSTRACT: Energy transfer between polystyrene donor and 2,5-diphenyloxazole (PPO) species incorporated as intramolecular energy traps has been studied by time-resolved luminescence spectroscopic techniques. It is demonstrated that the extent of energy transfer from excimeric species is negligible compared to that from unassociated (or monomeric) excited-state donors. The results implicate singlet energy migration in determination of the photophysical characteristics of polystyrene and in intramolecular energy trapping in polymers based on styrene derivatives.

Introduction

In the field of polymer photophysics the role of excimeric species in energy-transfer processes has been the subject of some speculation. Opinions have been expressed in the literature which cover the whole range of possibilities concerning energy transfer from polymers that exhibit both monomer and excimer emission, viz., that transfer occurs (a) solely from monomeric chromophores, (b) solely from excimeric entities, and (c) from both monomer and excimer species.

Hirayama et al.,[1] studying energy transfer to guest molecules in polystyrene, concluded that transfer occurred from monomeric phenyl chromophores. In contrast, Heisel and Laustriat[2] have concluded that transfer from excimer predominates the energy-transfer mechanism. Of relevance to the latter argument is the fact that Klöpffer[3] has indicated that transfer from monomeric species is at least feasible in polystyrene since transfer may be observed to residual styrene (from the polymerization process), whose absorption spectrum has negligible spectral overlap with the emission band of polystyrene excimer.

Several authors have indicated that energy transfer may occur from both excimer and monomer sites, including Powell[4] from studies on poly(vinyltoluene), Fox et al.[5] investigating intramolecular energy transfer in styrene–vinylnaphthalene copolymers, and David et al.,[6] who studied intermolecular energy transfer from polystyrene and a styrene–methyl methacrylate copolymer to tetraphenylbutadiene acceptor.

The studies discussed above were concerned in the main with the study of solid polymers. More recently, Aspler et al.[7] studying intramolecular energy transfer from naphthalene chromophores to anthracene acceptors in fluid solutions of 1-naphthyl methacrylate–9-vinylanthracene copolymers, concluded that energy transfer involves naphthalene monomeric sites as the sole donor species.

In the present paper we describe studies of intramolecular energy transfer in styrene polymers containing very small amounts of diphenyloxazole chromophore as acceptor with the following objectives: (a) to elucidate the dominant pathway for energy transfer in this system and (b) to gain information upon the excimeric trap concentration and its relationship to the existence of singlet energy migration in polymers. The incidence of energy migration and its importance in population of excimer sites in macromolecules has recently been disputed.[8]

Experimental Section

Materials. A sample of polystyrene containing 0.01 mol % 2,5-diphenyloxazole (PPO) chromophores as intramolecular energy traps was prepared by copolymerization of styrene and 2-phenyl-5-*p*-vinylphenyloxazole (POS) under high-vacuum conditions at 60 °C using AIBN as initiator. The polymer was purified by multiple reprecipitation.

The comonomer POS was synthesized according to Scheme I. Experimental conditions for the various reactions within the synthetic scheme have been detailed elsewhere.[9]

Methods. Two high-resolution time-resolved fluorescence spectrometers were employed in this study. In both cases conventional single-photon-counting detection methods were used. For excitation at 257.3 nm, the frequency-doubled, cavity-dumped output from a 4-W argon ion laser was used, resulting in excitation pulses of 7-ns duration at a repetition rate of 1 MHz. As a consequence of the high temporal stability of this system, however, deconvolution analysis is capable of resolving fluorescence decay times as short as ca. 500 ps. The spectrometer has been fully described elsewhere.[10]

For excitation at 308 nm, the second harmonic of a cavity-dumped, mode-locked, synchronously pumped dye laser was used, providing pulses of width <10 ps at a repetition rate of 4 MHz. This system, together with an evaluation of its capabilities, has been reported elsewhere.[11]

The data analysis procedures employed have been discussed at length in earlier reports.[12,13]

Fluorescence measurements were performed on thoroughly degassed dichloromethane solutions of optical density <0.1.

Results and Discussion

Total Fluorescence Spectrum. Figure 1 shows the total fluorescence spectrum of the sample of polystyrene labeled with 0.01% diphenyloxazole trap in degassed dichloromethane solution excited at 257.3 nm. Emission profiles characteristic of styryl monomer ($\lambda_{max} \sim 280$ nm), excimer ($\lambda_{max} \sim 330$ nm), and PPO ($\lambda_{max} \sim 370$ nm) are evident. The emission intensity of PPO exceeds that which can be accounted for in consideration of direct excitation alone and clearly indicates the existence of energy transfer from polystyrene donor.

Fluorescence Decays. (a) Direct Excitation of PPO Chromophore at 308 nm. The employment of 308-nm radiation from the synchronously pumped dye laser system allows determination of the fluorescence lifetime of PPO labels in the absence of energy-transfer effects that would result from excitation within the absorption band of polystyrene. Under these conditions, the fluorescence decay profile was found to be well described by use of a single-exponential function. The resultant lifetime (analyzed at 375 nm) was 1.68 ns.

(b) Excitation at 257 nm. Excitation at 257 nm results in absorption of energy by the phenyl groups of the

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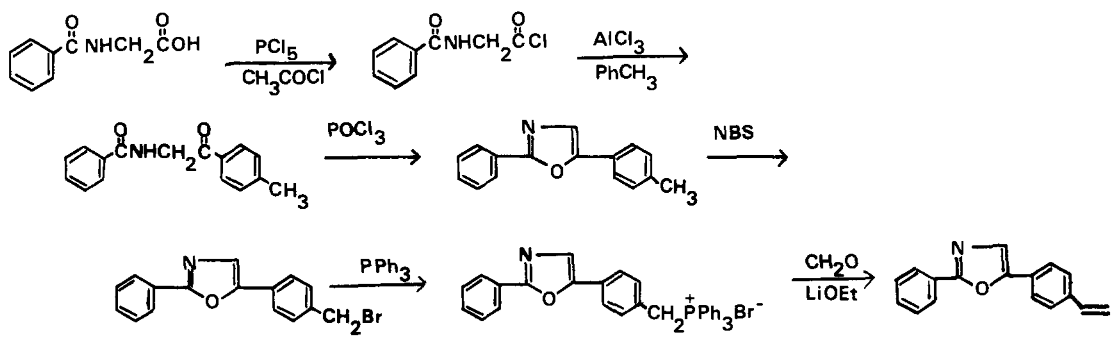
Scheme I



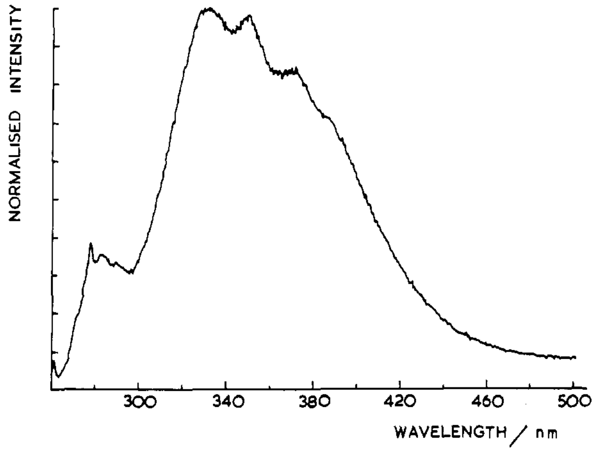


Figure 1. Total luminescence spectrum of polystyrene incorporating 0.01 mol % PPO (degassed CH_2Cl_2; 298 K; λ_{ex} = 257.3 nm).

polystyrene molecules and in a degree of direct excitation of PPO chromophores. Fluorescence decays were recorded at 290, 325, and 420 nm, corresponding to emissions principally originating from monomer, excimer, and label, respectively.

(i) Fluorescence Decays at 290 nm. Fluorescence decay curves in the region of monomer fluorescence were poorly described by single-exponential functions but well described by a dual-exponential fit using a function of the type

$$i(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \qquad (1)$$

where A_1 = 1.38, A_2 = 0.017, τ_1 = 0.68 ns, and τ_2 = 12.15 ns. The lifetimes are similar to values obtained previously[13] for pure polystyrene under identical experimental conditions but reflect the quenching influence of PPO consequent upon energy transfer from polystyrene, as will be discussed below. The fit to a double exponential and observation of a long decay time in the monomer emission are consistent with previous assertions that dissociation of excimer to re-form excited monomer occurs in polystyrene.[13]

(ii) Fluorescence Decays at 325 nm. Analysis of the decay data obtained at this wavelength is complicated by the considerable overlap of excimer and PPO fluorescence spectra. Equally acceptable fits ($\chi^2 < 1.1$) were obtained by using double- and triple-exponential functions $\sum B_i \exp(-t/\tau_i)$ with B_1 = 0.156, B_2 = 0.050, τ_1 = 14.83 ns, and τ_2 = 3.50 ns for a dual-exponential fit and B_1 = −0.167, B_2 = 0.153, B_3 = 0.161, τ_1 = 0.68 ns, τ_2 = 1.65 ns, and τ_3 = 14.7 ns for a triple-exponential fit. While the improvement in fit with a triple-exponential function relative to the double-exponential function is too slight to warrant adoption of the more complex function on statistical grounds, the triple-exponential data bear a degree of credibility for the following reasons: It is to be expected that two decay times common to those observed in the region of monomer decay with equal and opposite preexponential terms should be observed in the excimer decay of polystyrene.[13] A third decay time characteristic of the PPO label is also anticipated in the instance of spectral overlap. Comparison of the decay data obtained from a triple-exponential fit at 325 nm with those for monomer and directly excited PPO is encouraging in this respect.

In view of the difficulties in data analysis at this wavelength, no further use of these parameters was made in the kinetic treatment discussed later in this work.

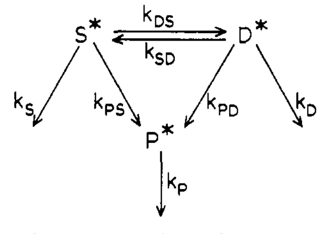


Figure 2. Photophysical reaction scheme.

(iii) Fluorescence Decays at 420 nm. Single- and dual-exponential functions were not capable of adequate description of the observed decay behavior in the region of PPO fluorescence. A triple-exponential fit of the form $\sum C_i \exp[-(t/\tau_i)]$ generated the following data with reasonable statistical confidence: C_1 = 0.700, C_2 = 0.033, C_3 = −0.225, τ_1 = 1.65 ns, τ_2 = 13.16 ns, and τ_3 = 0.70 ns.

The existence of decay components in the PPO emission characterized by τ_2 and τ_3 above, which are in good agreement with those characteristics of excimer and monomer from analysis of decays observed at 290 nm, implicates polystyrene species in the photophysical behavior of the PPO through the agency of energy transfer. The presence of the lifetime τ_1 is to be anticipated due to (a) a small contribution from direct excitation of PPO and (b) the existence of energy transfer from polystyrene as discussed below.

Photophysical Reaction Scheme. The observed kinetic data are consistent with the existence of one of the three photophysical reaction mechanisms depicted in the reaction scheme shown in Figure 2.

The individual kinetic schemes are differentiated as follows: (1) both styrene monomer and excimer act as energy donors to the PPO traps (k_{PS}, $k_{PD} \neq 0$); (2) energy transfer to PPO does not occur from the excimer (k_{PD} = 0); (3) energy transfer to PPO occurs solely from excimer (k_{PS} = 0).

Exact solution of the transient kinetics implied in the general reaction scheme shown in Figure 2 yields the following forms for the decays of monomer, $i_M(t)$, excimer, $i_D(t)$, and PPO, $i_P(t)$, respectively

$$i_M(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \qquad (2)$$

$$i_D(t) = A_3 \exp(-\lambda_1 t) + A_4 \exp(-\lambda_2 t) \tag{3}$$

$$i_P(t) = A_5 \exp(-\lambda_1 t) + A_6 \exp(-\lambda_2 t) + A_7 \exp(-\lambda_3 t) \tag{4}$$

where

$$\lambda_{1,2} = \tfrac{1}{2}[(X + Y + k_{PS} + k_{PD}) \pm \{(X + k_{PS} - Y - k_{PD})^2 + 4k_{DS}k_{SD}\}^{1/2}] \tag{5}$$

$$X = k_S + k_{DS} \tag{6}$$

$$Y = k_D + k_{SD} \tag{7}$$

and

$$\lambda_3 = k_P \tag{8}$$

A_i (i = 1–7) are functions containing terms involving individual rate constants and initial excited-state concentrations.

Due to spectral overlap at 325 nm, the experimentally observed decay profile at this wavelength will consist of a combination of eq 3 and 4, while $i_{290}(t)$ and $i_{420}(t)$ will correspond closely to $i_M(t)$ and $i_P(t)$ as described in (2) and (4), respectively. The empirical data listed above are in agreement with the forms of decay functions predicted by the reaction schemes. In particular, it is interesting to note that the signs of A_5, A_6, and A_7 do not permit distinction between the three individual reaction mechanisms incorporated within our general photophysical scheme.

Time-Resolved Emission Spectra (Figure 3). The early-gated spectrum (a) is dominated by fluorescences from styrene monomer and PPO excited directly. As the time delay between excitation and analysis is increased, a growth of excimer band relative to those of monomer and PPO is observed. Furthermore, once the time delay following the onset of excitation exceeds the excitation pulse width (7 ns), a marked decrease in the component ascribable to monomer is apparent (spectrum e). In late-gated spectra, (g) and (h), the profile has approached a relatively constant shape dominated by excimer emission. The residual monomer fluorescence is indicative of the existence of reversal to excited monomer by dissociation of styrene excimers.[10] Comparison of the late-gated profile of spectrum h with that of a pure polystyrene homopolymer (Figure 4) reveals the existence of enhanced fluorescence in the low-energy tail of the emission profile. The identity of the species responsible for this emission is revealed by the form of the difference spectrum between the late-gated emissions of labeled and pure polystyrenes. It is obvious that PPO emission is being observed when one compares the difference spectrum with those of (i) directly excited PPO label or (ii) the low-energy portion of the early-gated spectrum, (a). These spectra provide unambiguous evidence for population of PPO traps by energy transfer from polymer since the resultant emission is observed on a time scale characteristic of the polystyrene excimer. The nature of the involvement of excimer is not apparent from these spectra alone since a component of PPO decay of lifetime characteristic of excimer will result from either (i) direct transfer from excimer to PPO or (ii) transfer from excited monomer that has been generated by reverse excimer dissociation. However, inspection of the late-gated spectrum allows some insight into the role of the excimer in the process of energy transfer to PPO based on the following argument. Since (i) the overlap integral between excimer fluorescence and PPO absorption is greater than that for monomer emission and trap absorption and (ii) the PPO emission is relatively weak in the presence of high excimer emission intensity relative to that of monomer, it is tempting to construe that the excimer plays a lesser part in excited-state PPO population relative to monomer. Confirmation of this intuitive reasoning requires a more rigorous approach through examination of the transient kinetic data as discussed below.

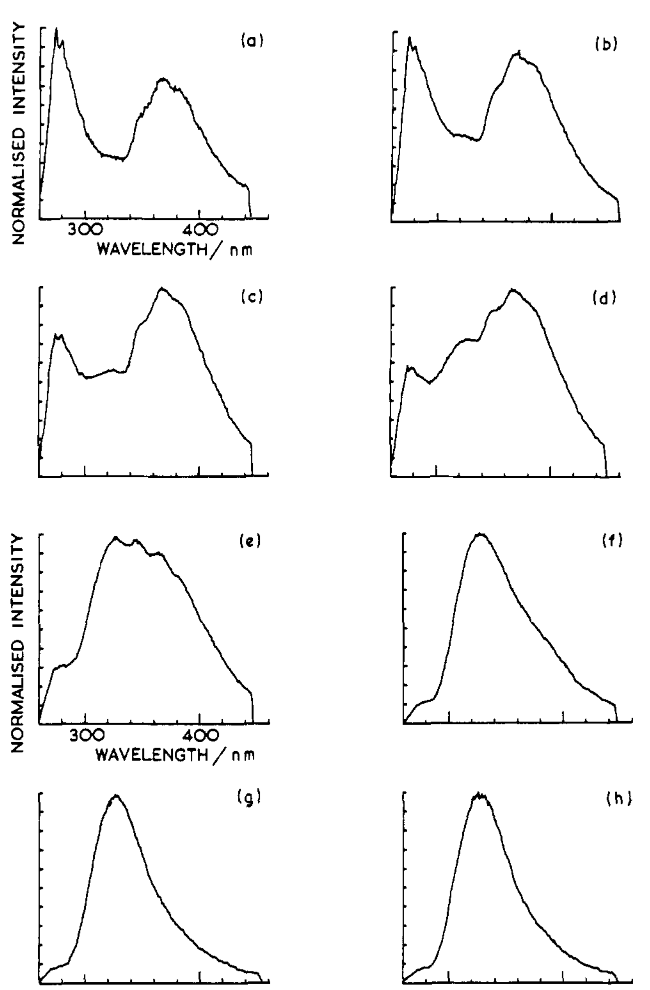


Figure 3. Time-resolved fluorescence spectra of PPO-labeled polystyrene (degassed CH_2Cl_2; 298 K; λ_{ex} = 257.3 nm): spectra recorded at (a) 0, (b) 3.2, (c) 6.4, (d) 9.6, (e) 12.8, (f) 15.0, (g) 18.2, and (h) 21.4 ns after excitation.

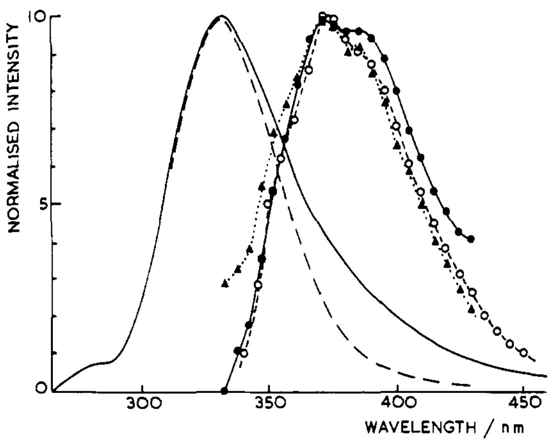


Figure 4. Late-gated time-resolved spectra of polystyrene (---) and the PS/POS copolymer (—). Shown for comparison are the difference spectrum between these late-gated spectra (●), the spectrum of the PPO label obtained from the early-gated time-resolved emission profile (▲), and the spectrum of PPO obtained by direct excitation at 308 nm (○).

Examination of the Relative Importance of Polystyrene Excimer and Excited Monomer as Energy Donors. From eq 5 it may be shown that

$$\lambda_1 + \lambda_2 = (X + Y) + k_{PS} + k_{PD} \tag{9}$$

and

$$\lambda_1\lambda_2 = (X + k_{PS})(Y + k_{PD}) - k_{DS}k_{SD} \qquad (10)$$

In the absence of an energy-accepting label (i.e., in pure polystyrene), the decay behavior may be characterized by two decay parameters,[13] λ_1^0 and λ_2^0, where

$$\lambda_1^0 + \lambda_2^0 = X + Y \qquad (9a)$$

and

$$\lambda_1^0\lambda_2^0 = XY - k_{DS}k_{SD} \qquad (10a)$$

Combination of eq 9 and 9a and eq 10 and 10a allows generation of two simultaneous equations and thereby solution for the two unknown coefficients, k_{PS} and k_{PD}, since X, Y, k_{SD}, k_{DS}, λ_1^0, and λ_2^0 are known from our previous studies on the photophysical behavior of polystyrene[13] and λ_1 and λ_2 are afforded by the present experiments. The resultant values are $k_{PS} = 3.6 \times 10^8$ s^{-1} and $k_{PD} = -0.05 \times 10^8$ s^{-1}.

While the negative value of k_{PD} is meaningless, it should be noted that the cumulative experimental error involved in combination of the empirical rate parameters is such as to exceed the magnitude of the derived rate coefficient k_{PD}. It can be said that k_{PD} is effectively zero or at least small compared with k_{PS}.

This conclusion is substantiated by an approximation to k_{PS}/k_{PD}, which is afforded by the following less rigorous approach:

If it is assumed that $4k_{DS}k_{SD} \ll (X - Y)^2$ then

$$\lambda_1 \sim \lambda_1^0 + k_{PS} \qquad (11)$$

and

$$\lambda_2 \sim \lambda_2^0 + k_{PD} \qquad (12)$$

This approach gives

$$k_{PS}/k_{PD} \simeq 30$$

Existence of Energy Migration in Polystyrene. Recently, MacCallum[8,14] has made the valuable observation that while singlet energy migration to trap sites such as potential excimer configurations and other types of energy sink has been generally accepted in the scientific literature, the concept lacks the security that would result from the design of a definitive experiment in this area. The data presented in the work are of direct relevance to this issue and, as discussed below, provide evidence for the existence of singlet energy migration independent of that furnished by emission anisotropy experiments (see, for example, ref 15–18) and the ability of functions descriptive of copolymer microcomposition, derived (see, for example, ref 17 and 18) on the assumption that migration exists, to describe the concentration dependence of macromolecular photophysical behavior (see, for example, ref 17–21). The validity of the emission depolarization data has been challenged, while the failure of the fitting of the photophysical data to microcompositional terms to demonstrate the existence of energy migration in an unambiguous manner has been asserted.[14] Resolution of the issue regarding energy migration is fundamental to the understanding of polymer photophysics and consequent photochemical behavior. The existence of migration differentiates the situation in which macromolecular systems represent somewhat unique photophysical entities from that in which the polymer merely acts as an assemblage of chromophores that rely upon their highly concentrated local environment as the sole discriminator of their photoactivity from that of low molar mass species.

The data presented earlier in this paper offer strong evidence for the existence of energy migration in styrene polymers. The reasoning that leads to this conclusion is detailed below.

If we assume at the outset that energy migration does not occur in polystyrene, then energy is localized at the chromophore at which absorption occurs, and excimer emission results solely from sites that can adopt the required orientation during the excited monomeric lifetime. As a consequence, it would have to be argued that the ratio of excimer to monomer fluorescence yields revealed in the fluorescence spectrum of the homopolymer reflects the influence of the twin parameters of relative concentration and quantum efficiency of emission of excimer and monomer. Since the emission spectrum of dilute solutions of polystyrene are dominated by fluorescence from intramolecular excimer sites, the logical conclusion in the absence of migration is that excimeric species are relatively abundant and exhibit reasonably high fluorescence efficiency in the polymer. However, these factors allied to the relatively long-lived nature of the excimer and the considerable degree of spectral overlap with the PPO absorption band would produce reasonably efficient energy transfer from excimer donors to PPO traps. Since this is incompatible with the observed kinetic behavior, it must be concluded that the initial assumption of energy localization is wrong.

The relatively minor contribution to the energy received by PPO traps from the excimer implies that intramolecular excimeric species are present in relatively low concentrations in polystyrene. The large contribution to the emission profile made by the excimer must therefore result from energy migration and subsequent trapping at excimer sites in the polymer chain.

Conclusions

(1) In intramolecular energy transfer to guest traps in polystyrene the excimer plays an insignificant role as a donor relative to that of excimer monomer.

(2) Energy migration occurs in polystyrene.

(3) Quantitative evaluation of the mechanism of intramolecular energy trapping could only be made subsequent to the determination of the photophysical behavior of pure polystyrene.[13] This observation emphasizes the need to study fundamental photophysics in polymer systems if it is desired that a complete picture of polymer photochemistry (which implies understanding of energy trapping by photolabile species) be obtained.

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Registry No. Styrene/2-phenyl-5-(*p*-vinylphenyl)oxazole copolymer, 64652-65-9.

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Transient Decay Studies of Photophysical Processes in Aromatic Polymers. 7. Studies of the Molecular Weight Dependence of Intramolecular Excimer Formation in Polystyrene and Styrene–Butadiene Block Copolymers

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ABSTRACT: A series of styrene homopolymers and styrene–butadiene block copolymers of type SB and SBSB in which the sequence length of styrene chromophores has been varied has been studied by time-resolved fluorescence techniques. It has been shown that the kinetic behavior of polystyrene fluorescence cannot be attributed to the existence of kinetically distinct monomeric species. The dual-exponential decays observed in the region of monomer emission are assigned to the influence of quenched monomer and excimer dissociation, respectively. The molar mass dependence of the polystyrene photophysics is best explained by models that assume energy migration to occur within (and, at low molecular weights, to be limited by) the chromophore sequence lengths.

Introduction

While there has been an increased recognition that the photophysical behavior of macromolecules is not, in general, conducive for analogous small-molecule systems, the complex microheterogeneity of polymers has hindered agreement upon interpretation of the resultant kinetic data. In general, it is to be anticipated that the transient decay kinetics will require adoption of several decay coefficients for adequate description. The various models that have been proposed[1-7] differ principally in the identification of photophysical sites that are responsible for the dominant averages observed in the kinetic behavior. More fundamental question arise regarding the role and existence of energy migration in excimer formation. The subject has been recently reviewed.[8]

The decay kinetics of fluid solutions of polystyrene are less complex than those exhibited by other vinyl aromatic polymers[1,2] since the decay of excited monomer may be described in terms of a dual-exponential function.[9,10] As the heterogeneity of the chain microcomposition is increased through incorporation of randomly distributed spectroscopically inactive comonomer at varying intramolecular concentrations, the decay kinetics become more complex. This latter fact establishes credibility for mechanisms that impute[1-3] the involvement of excited-state monomeric entities that display a degree of isolation within the kinetic scheme relative to excited monomer subject to enhanced quenching through excimer formation. The absence of geometric isolation in polystyrene and the consequent simplification of the kinetics facilitate investigations of the factors governing excimer formation and testing of the validity of proposals regarding the nature of the excitation sites.

In previous reports we have shown that the intramolecular concentration dependence of excimer formation in certain polymers may be adequately described in terms of functions that incorporate terms descriptive of both energy migration and potential excimer site concentration.[1,2,9,11,12] In the case of one such function, involving mean chromophore sequence length and fraction of pairs of aromatic units, it has been suggested that energy migration need not be invoked in its derivation.[6,7] The alternative derivation implies differential photophysical activity between units that are centered in chromophoric sequences and those situated at the end of chromophoric blocks. Similar reasoning has been employed[6] to explain the observed molar mass dependence of the degree of excimer formation[13] in polystyrene.

In this paper we report investigations of the transient photophysical behavior of "monodisperse" polystyrene of varying molar mass and block styrene–butadiene copolymers of varying chromophore sequence length of both the type SB, containing a single block of styrene units, and the type SBSB, containing two styrene blocks. The results are pertinent to considerations of (1) the nature of the molecular weight dependence of excimer formation in polystyrenes, (2) the role of energy migration within blocks of chromophores in the excimer formation mechanism, (3) the question of distinctly different photophysical activity at sequence termini relative to chromophores situated within blocks, and (4) the extent to which long-range excimer interactions may occur as a result of either intrachain segmental or energy diffusion between blocks in copolymers containing more than one chromophoric sequence length. It has been inferred that the latter mechanism is of little significance in macromolecular

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