The Effect of Molecular Weight on Triplet Exciton Processes. 3. Quenching of Poly(2-vinylnaphthalene) Delayed Emission by Piperylene

N. F. Pasch, R. D. McKenzie, and S. E. Webber*

Department of Chemistry, University of Texas, Austin, Texas 78712.

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ABSTRACT: The efficiency of piperylene quenching of phosphorescence and delayed emission of different molecular weight samples of poly(2-vinylnaphthalene) is shown to increase with molecular weight. We interprete this finding as demonstrating that increasing the polymer length allows a triplet exciton more opportunities to encounter a quencher until the polymer length exceeds the exciton diffusion length (approximately 700 chromophores for poly(2-vinylnaphthalene)). All experiments reported are for 1:1 THF–Et_2O matrices at 77 K.

I. Introduction

Since 1969[1] there have been reported a number of studies of triplet excitons in 77 K matrices. Polymers studied include poly(1-vinylnaphthalene),[1,2] poly(acenaphthalene),[3] poly(naphthyl methacrylate),[4,5] poly(*N*-vinylcarbazole),[6,7] and poly(2-vinylnaphthalene).[8] For the latter two polymers the intensity of delayed fluorescence and phosphorescence were shown to be dependent on molecular weight. Pasch and Webber[8] and Klöpffer et al.[7] argued that this dependence arises from the increased probability of multiple exciton occupation of a single chain as the length of the polymer increases.

Another manifestation of triplet energy transport in polymers is the much larger quenching rate of triplet state luminescence relative to monomeric model compounds. David et al.[3] have fit the quenching of phosphorescence in poly(acenaphthalene) to the Stern–Volmer equation and used the rate constant to estimate the triplet exciton transfer rate between chromophores. This method has been applied to poly(1-vinylnaphthalene) by Cozzens and Fox[1] and to poly(naphthyl methacrylate) by Somersall and Guillet.[4] The transfer rates for polymers in glassy matrices derived in this fashion have been in the range of 128 to 300 s^{-1}.

We wish to report the results of a quenching study of delayed fluorescence and phosphorescence for samples of poly(2-vinylnaphthalene) (P2VN) that show that the efficiency of triplet exciton quenching increases with chain length. One simple explanation of this effect is that for a longer polymer chain a larger volume of the matrix containing quencher can be "sampled" by the exciton. No further change with molecular weight is expected when the polymer chain length exceeds the exciton diffusion length, L_D ($L_D = (D_{ex}\tau_T)^{1/2}$, where D_{ex} is the exciton diffusion constant and τ_T is the triplet state lifetime). An analysis of the quenching of triplet excitons is complicated by the fact that a luminescing sample is composed of a distribution of species with respect to: (1) molecular weight, (2) number of excitons on polymer chains of a given length, and (3) number of quencher "contacts" with the polymer that can lead to quenching (and of course there will be a distribution of quencher–chromophore separations). In (2), and possibly (3), the average numbers of excitons or quencher contacts per chain may be small such that one cannot use a "central value limit" in evaluating theoretical quantities. For example, polymers with one or two excitons may be quenched differently for a given number of quencher contacts because in the latter case bimolecular annihiation may dominate the decay rates. In addition, excitons may self-trap such that the triplet state population may be composed of mobile triplet excitons and trapped triplet molecules, each with a distinctly different quenching rate.

Despite the complexity of a theoretical model for the quenching process at this stage of our understanding of triplet excitons in polymers we believe that the observation of a molecular weight effect on quenching rates adds a new feature to this field that must be taken into account in future work. Certainly it shows that comparisons of quenching rates for two different polymers can be very misleading if they differ significantly in their molecular weight.

II. Experimental Section

The P2VN samples were those used in an earlier report.[8] All solutions were $1.0 \pm 0.15 \times 10^{-3}$ M in the naphthalene chromophore. The solvents were carefully purified by refluxing over $LiAlH_4$ in a nitrogen atmosphere and distilling just before use. A 1:1 mixture of tetrahydrofuran (THF) and diethyl ether (Et_2O) formed a clear glass at 77 K and would easily dissolve the polymer. A mixture of cis, trans isomers of piperylene (Aldrich, P-4985-6) was fractionally distilled several times and checked for clarity in the UV and for the absence of a delayed emission at 77 K (in a THF–Et_2O glass). A slight delayed luminescence from the piperylene was detectable at 0.1 M with this purification, but our quenching studies cover a piperylene concentration from approximately 0.005 to 0.08 M such that this impurity emission did not interfere.

Delayed emission spectra of the different molecular weights and variable concentration of piperylene were essentially identical except for the overall absolute intensity and the relative intensity of the delayed fluorescence. Excitation was effected by a 200-W high-pressure mercury lamp and a Corning 7-54 UV transmitting filter. We have estimated the triplet density to be $\sim 10^{-2}$ chromophore/chromophore. For the intensity measurement the photomultiplier signal waveform was signal averaged using a set photomultiplier voltage and varying the input sensitivity and number of scans accumulated. This waveform yields the intensity of the delayed emission at a time near the cessation of excitation and the decay of the delayed emission yields an approximate decay rate over a 2.4-ms period. For the present samples the decay of the phosphorescence during this period is negligible. The reproducibility of the absolute intensity using this technique was found to be approximately 2–4% from day to day. The intensity of delayed fluorescence was determined at 340 nm and phosphorescence at 520 nm.

Samples were prepared as follows: (1) a $\sim 10^{-2}$ M solution of the polymer is prepared by direct weighing, (2) this solution is diluted to 1.0×10^{-3} M (checked by the absorption spectrum), and (3) piperylene is added with a micropipet. All containers and sample tubes (4-mm o.d.) were quartz and were cleaned by soaking in hot 50% HNO_3, followed by rinsing in distilled water, and then pyrolyzed to remove any organic residue. All samples were subjected to 3 freeze–pump–thaw cycles on a $\sim 10^{-5}$ Torr vacuum line before sealing.

III. Results

The primary effect observed was that mentioned in the Introduction: the degree of luminescence quenching for a given concentration of quencher increased remarkably with molecular weight. In Figure 1 we have presented the quenching of phosphorescence as $I_{Ph}(Q)^{-1}$ ($I_{Ph}(Q)$ = intensity of phosphorescence in presence of concentration [Q] of

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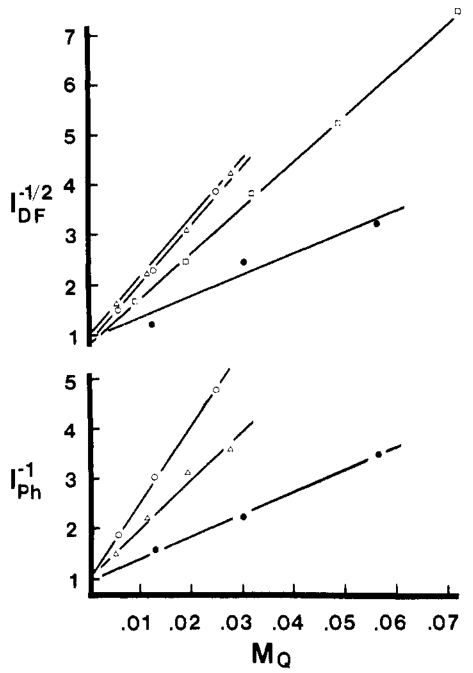

Figure 1. Quenching of phosphorescence, delayed fluorescence, plotting according to Stern–Volmer kinetics: (○) polymer **6**, $P = 3250$; (△) polymer **2c**, $P = 664$; (□) polymer **2b**, $P = 273$; (●) polymer **1a**, $P = 100$ (see Table I).

Table I
Quenching Rates[a] of Polymers with Different Degrees of Polymerization

Polymer[b]	$\bar{P}$[b]	k_{Ph},[c] M^{-1}	k_{DF},[c] M^{-1}	ω_{av},[d] s^{-1}
1a	100	42.8	41.3	57.8
2b	273	*e*	90.0	124.0
2c	664	94.9	97.9	132.0
6	3250	150.0	116.0	183.0

[a] Rates in terms of Stern–Volmer equation $I(0)/I(Q) = A + k_Q[Q]$, where $A = 1.0$ for exact agreement with SV kinetics. In the least-squares fit A varied from 0.87 to 1.10 for the above data. [b] Polymer designation and $\bar{P}$ (degree of polymerization) as given in ref 8. [c] For k_{Ph} (phosphorescence quenching) $I_{Ph}(Q)^{-1}$ was fit to a straight line; for k_{DF} (delayed fluorescence quenching) $I_{DF}(Q)^{-1/2}$ was fit to a straight line. [d] Calculated according to eq 1 and 2 where the average k_Q for phosphorescence, delayed fluorescence used, and $\tau_T = 2.1$ s are assumed. These values are presented for comparison to previously published values and within the set; we do not believe ω to represent a simple, intrinsic exciton-transfer rate. See text. [e] Samples accidently destroyed before phosphorescence could be run and supply of polymer was exhausted.

quencher) and the quenching of delayed fluorescence as $I_{DF}(Q)^{-1/2}$. For a homogeneous solution where $I_{Ph} \propto [T]$ and $I_{DF} \propto [T]^2$ these two plots should be identical. We ascribe the fact that they are not identical to the complications of the "ensemble" of multiply and singly excited polymer chains. Within the accuracy of the data both quenching curves follow Stern–Volmer kinetics, with slightly different quenching rates (see Table I).[9] Using the same analysis as David et al.[3]

$$k_Q = (4\pi N_0 D_{ex} R_0 \times 10^{-3})\tau_T \text{ L mol}^{-1} \qquad (1)$$

where τ_T is the triplet lifetime, approximately 2.1 s for naphthalene groups on the polymer, $N_0 = 6.023 \times 10^{23}$ mol^{-1}, R_0 = "critical triplet transfer separation" for naphthalene–piperylene, and D_{ex} = diffusion constant for triplet energy migration between chromophores. Following David et al.[3] and Somersall and Guillet,[4] we take R_0 to be 11 Å, which yields a value of D_{ex} for phosphorescence quenching and delayed fluorescence quenching. These same authors related D_{ex} to the exciton transfer rate, assuming a chromophore separation ($\bar{r}$) of 5 Å, as follows[10]

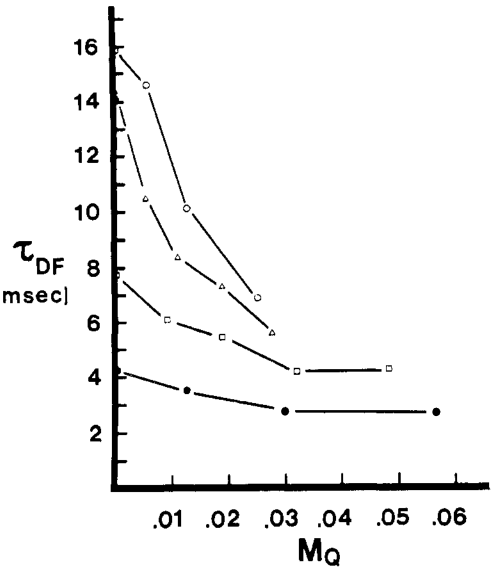

Figure 2. Lifetime of delayed fluorescence (from eq 3 of text) as a function of quencher concentration. Same symbols as in Figure 1.

$$\omega = 6D_{ex}/\bar{r}^2 \qquad (2)$$

from which the values of ω in Table I have been derived, for comparison with the earlier data. Note that this formulation does not explicitly depend on the length of the polymer chain.

In Figure 2 are presented the variations in τ_{DF}, where

$$\tau_{DF} = t_{obsd}/\ln\,(I_{DF}(0)/I_{DF}(t_{obsd})) \qquad (3)$$

t_{obsd} is the observation period for the choppers (2.4 ms), and $I_{DF}(t)$ is the time-dependent delayed fluorescence signal[11] (the phosphorescence decays so little during t_{obsd} that accurate values of τ_{Ph} are impossible to obtain). As can be seen from Figure 2 the relative change of τ_{DF} with quencher was much larger for the higher molecular weight polymers. Our interpretation for the faster rate of DF decay for lower molecular weights has been the following: if a lower molecular weight polymer is multiply excited the average separation of the excitons is smaller than for multiply excited polymers of the higher molecular weights.[12] Hence the biomolecular decay process is less rapid in the latter. Moreover if the average exciton separations increase with the molecular weight of the polymer, there is greater opportunity for quenching to occur before exciton annihilation can occur. The values of τ_{DF} seem to be approaching an asymptotic limit, especially for the lower molecular weight samples, even though intensity of delayed fluorescence continues to be quenched (in the usual case for SV kinetics the change in τ_{DF} should follow the quenching of emission). We interpret this as follows: polymers with a larger number of contacts with quencher have such a low quantum efficiency of emission that these polymers make virtually no contribution to the observed decay function.[13] One would expect that as [Q] continues to increase that the τ_{DF}'s would become equal for all molecular weights (but the poor S/N ratio would make an accurate measurement difficult).

As mentioned in the Introduction, our interpretation of this molecular weight effect is that a triplet exciton on a larger polymer can sample a larger volume of the matrix, with an increased opportunity to encounter quencher molecules. One may define the diffusion length of a triplet exciton by

$$L_D\,(\bar{r}^2)^{1/2} = (D_{ex}\,\tau_T)^{1/2} = (\bar{r}^2)^{1/2}(\tau_T\omega)^{1/2} \qquad (4)$$

where L_D = the number of chromophores in the exciton diffusion length, $\bar{r}^2$ = the average of the square of the chromophore separation, and ω = the reciprocal of the average exciton transfer time between chromophores. Once the average polymer length exceeds L_D there should be no further effect of molecular weight. Since our quenching results and previous spectroscopic observations[8] tend to "saturate" for a degree of polymerization of approximately 650–700 and τ_T = 2 s, the value of L_D = 650–700 implies a τ_{trans} of approximately 5×10^{-6} s, much faster than estimated from the quenching formula discussed above (see Table I), but still five to six orders of magnitude smaller than for molecular crystals. Obviously a more direct method for determining triplet exciton transfer rates than quenching experiments is highly desirable.

Our proposed interpretation of our observations is not the only possibility. For example, one could suppose that the rate of triplet exciton transfer systematically increases with higher molecular weight because of some steric effect. Possibly the lower density of a higher molecular weight polymer coil in a 77 K matrix allows an increased number of contacts with quencher molecules per unit length of the polymer chains. The primary reason we propose the above interpretation in terms of an exciton diffusion length is that it seems to be consistent with the molecular weight dependence of triplet–triplet annihilation processes in P2VN.[8] One clear implication of our experimental results is that if triplet excitons were to be exploited to sensitize a photochemical process in matrices then a higher molecular weight polymer would be expected to be more effective. Experiments are planned for the future to study the molecular weight dependence for triplet exciton quenching in fluid solution.

One further observation we have made is quite puzzling. After a period of months samples containing piperylene developed a new "impurity" delayed emission around 400 nm; this impurity did not appear in the unquenched samples. Furthermore the intensity of this impurity emission was much stronger in the solutions containing high molecular weight polymer. These samples were stored in subdued light at room temperature. At present we do not know the origin of this new emission feature.

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References and Notes

(1) R. F. Cozzens and R. B. Fox, *J. Chem. Phys.*, **50**, 1532 (1969).

(2) See papers by R. B. Fox and co-workers, starting with ref 1. More recently see R. B. Fox, T. R. Price, R. F. Cozzens, and W. H. Echols, *Macromolecules*, **7**, 937 (1974), and references therein.

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(7) W. Klöpffer, D. Fischer, and G. Naundorf, *Macromolecules*, **10**, 450 (1977).

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(9) In ref 4 it was found that the quenching of the DF could be fit to a Perrin model and the phosphorescence to Stern–Volmer kinetics.

(10) Equation 2 is valid for three-dimensional diffusion. Presuming that one-dimensional diffusion is more appropriate to this problem, the relation should be $\omega = 2\lambda/\bar{r}^2$ (see S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943)). We use eq 2 to allow a direct comparison to the values obtained by David et al. (ref 3) and Somersall and Guillet (ref 4).

(11) If the decay of DF were exponential the τ_{DF} would be the lifetime of DF. Since the decay we observe is generally not exponential, τ_{DF} is a relative measure of the extent of signal decay during the 2.4-ms observation time.

(12) This argument can be illustrated by an example. If we compare two polymers of length L and $2L$ the probability of doubly exciting the latter is twice as great as the former. However, for those polymers of length L that do happen to be doubly excited, the average exciton separation is half that of the polymer of length $2L$. A manuscript dealing with exciton densities in one-dimensional lattices is in preparation.

(13) This argument is like the Perrin model: A quenched molecule is quenched so quickly that its lifetime becomes essentially zero; however, the luminescence decays at the rate of an unquenched molecule because those molecules that are quenched make essentially no contribution to the luminescence. Hence for this model a quenching of intensity is possible without changing the luminescence decay rate.

Photo- and Radiation-Induced Degradation of Vinyl Polymers in Solution. 2. Photosensitized Degradation of Poly-α-methylstyrene by Benzophenone

Tomiki Ikeda,[1a] Koji Kawaguchi,[1a] Hitoshi Yamaoka,* [1b] and Seizo Okamura[1a]

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan, and Research Reactor Institute, Kyoto University, Kumatori 590-04, Osaka, Japan.

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ABSTRACT: The photosensitized degradation of poly-α-methylstyrene (PMSt) by benzophenone (BP) was studied at 30 °C in benzene solution using 366-nm light. Random scission of the polymer chain was confirmed by GPC measurements. The quantum yield for main-chain scission (ϕ_s) was found to be independent of incident light intensity and greater than that of direct photolysis. On adding a small amount of a triplet quencher (naphthalene), ϕ_s decreased with increasing added quencher concentration. The degradation was found to be initiated by hydrogen abstraction from PMSt main chain by excited triplet BP and the rate constant of this reaction was estimated to be 9×10^3 M^{-1} s^{-1} on the basis of kinetical treatment. The effect of oxygen on the degradation was also discussed.

Extensive studies on photodegradation of polystyrene have been made by many workers.[2] However, little attention has been paid to poly-α-methylstyrene which is well known as a typical degradation-type polymer.

Fox et al. first investigated the photodegradation of PMSt by 253.7-nm light and reported the quantum yield for main-chain scission.[3,4] Their observed values in inert solvents were fairly low compared with those of ketone polymers, e.g., poly(phenyl vinyl ketone),[5] though PMSt itself is a strong absorber of light at the irradiated wavelength.

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