

acetone triplet (3K) is slightly lower than that of the triplet of a pendant phenyl group ($E_T \approx 78$ kcal/mole ≈ 27200 cm^{-1} versus ≈ 81 kcal/mole ≈ 28400 cm^{-1} , respectively) thermal activation of ≈ 3 kcal/mole is needed to generate triplet excitons in polystyrene if TMD is used as an energy source.

Poly-N-vinylcarbazole (PVCA), on the other hand, possesses [5] a much lower triplet ($E_T = 68$ kcal/mole ≈ 23800 cm^{-1}) than 3K . As a result, the energy transfer processes ${}^3K + \text{PVCA} \rightarrow K + {}^3\text{PVCA}$ is exothermic and is expected to occur efficiently. With this idea in mind we have studied triplet exciton migration in PVCA by (a) generating 3K from TMD, (b) generating excitons in PVCA by energy transfer from 3K to PVCA, (c) trapping the excitons irreversibly with triplet acceptors which are capable of emitting phosphorescence.

2. Experimental methods

TMD was prepared by a published procedure [11]. 1,4-dibromonaphthalene (DBN, Eastman) was purified by recrystallization. 1,10-phenanthroline (PHTH, Aldrich) was purified as follows. One gram of PHTH in 10 ml methylene chloride was passed through a basic alumina (Fisher, Brockman activity 1) column (20 cm in length, 1.5 cm in diameter) and an extra 250 ml CH_2Cl_2 was used as an elution solvent. The PVCA (Luvican M170, BASF) was reprecipitated by methanol from benzene solution. Benzene solutions containing PVCA, dioxetane (usually $\approx 3 \times 10^{-2}\text{M}$) and either DBN or PHTH were prepared by rotating aluminum foil covered vials for about 2 h at room temperature. One gram of this solution was spread on a surface-benzene-saturated microscope slide with a glass frame on the edge. The slide was placed in a benzene-vapor rich box (to retard evaporation of the solvent) about 4 h before drying in vacuo. The thickness of a dry film was approximately 10 μm . A portion of a film was sandwiched between an aluminum foil wrapped stainless steel block and a thin stainless steel strip having a hole 8 mm in diameter. The sample was degassed with a vacuum pump at 10^{-2} torr for 1 h, saturated with argon, and kept at $34 \pm 0.5^\circ\text{C}$ throughout the measurement. A phototube (EMI 9813 QA) equipped with a Jarrell-Asch 1/4 meter monochromator was employed to measure the chemiluminescence derived from the PVCA films. After the sample had been

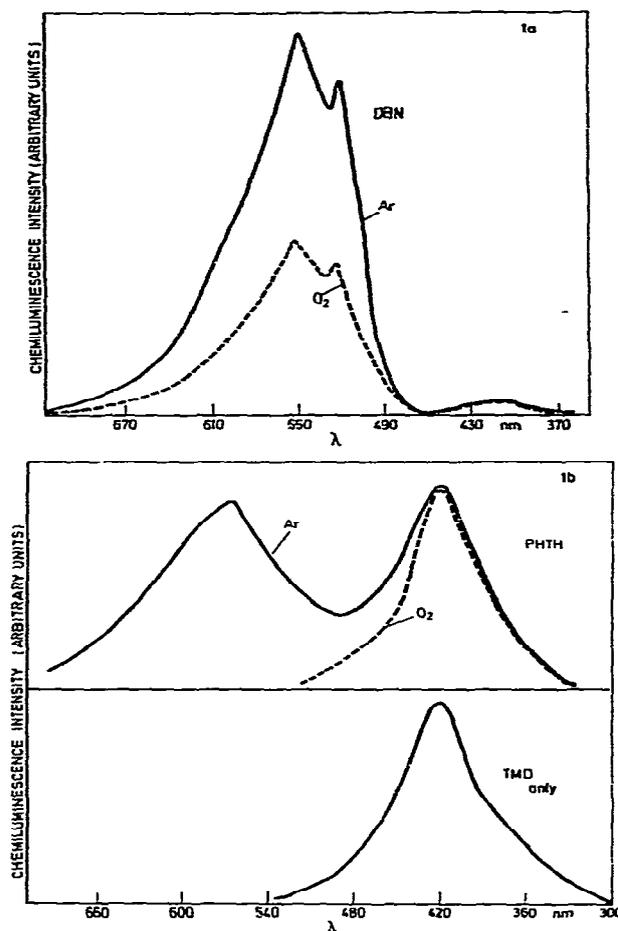


Fig. 1. Chemiluminescence from PVCA films containing TMD and DBN (emission slit 5 nm) or PHTH (emission slit 40 nm), measured by Perkin-Elmer fluorescence spectrophotometer MP7-3L equipped with Hamamatsu PMT, R77710, uncorrected. Temperature 34°C .

warmed up to the desired temperature, the intensity of chemiluminescence was constant for a period of one hour or more. This observation implies a constant rate of 3K formation throughout the measurement.

Direct chemiluminescence (pure acetone fluorescence) is observed upon heating of PVCA films containing TMD. No phosphorescence attributable to PVCA could be detected. Addition of DBN or PHTH to PVCA films containing TMD results in the generation of indirect chemiluminescence of the energy acceptors (fig. 1). No emission was observed under the same experimental conditions upon heating PVCA films alone or

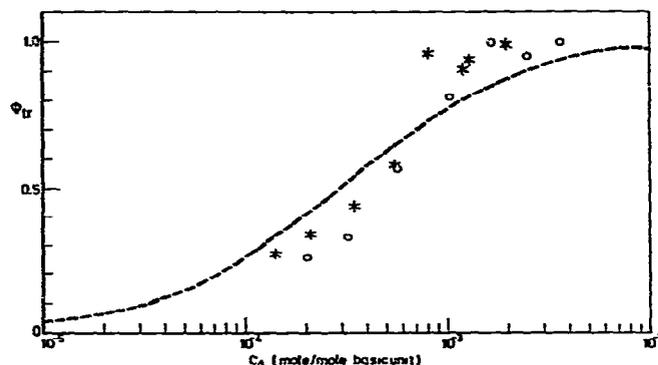


Fig. 2. Chemiluminescence intensity of DBN (\circ) and PHTH ($*$) acceptors as a function of acceptor concentration. Data plotted according to eq. (4) (exciton migration model).

upon heating PVCA containing DBN or PHTH. Thus, TMD is clearly needed to provide an energy source for chemiluminescence. As can be seen from fig. 1a, the phosphorescence of DBN is not completely quenched by oxygen, in contrast to the behavior of PHTH (fig. 1b).

This discrepancy as well as the relative weakness of the PHTH signal can be explained by the strongly different triplet decay times of the two additives, PHTH: $\tau_p = 1.6$ s [15], DBN: $\tau_p = 1$ to 3 ms in purest crystals [16] (1-bromonaphthalene in ethanol/ether at 77 K has a decay time of $\tau_p = 20$ ms [17]).

The triplet state of PHTH is expected to be quenched partially by oxygen traces under argon due to its long lifetime whereas the short lived triplet of DBN cannot be quenched completely, even if oxygen diffuses into the polymer.

The relative intensity of indirect chemiluminescence was measured as a function of acceptor concentration. The data are plotted in fig. 2 as ϕ_{tr} (discussed below) versus the log of the concentration of acceptor.

3. Treatment of the data. The Perrin model and the exciton hopping model

Four models have been commonly employed to derive energy transfer parameters from data obtained in rigid media [12]: (1) the Perrin model, (2) the exciton hopping model, (3) the Förster model and (4) the Stern–Volmer model. Since we are dealing with triplet–triplet energy transfer, the Förster model seems inappropriate. The Stern–Volmer (molecular diffusion) model assumes complete statistical mixing of

donor and acceptor molecules during the donor lifetime; this model is not appropriate for media in which diffusion is prohibited. The Perrin model [13] assumes no specific mechanism for energy transfer, but postulates the existence of a “quenching sphere” containing an excited donor molecule. If a quencher molecule exists within this sphere, the model assumes 100% quenching efficiency and if a quencher molecule exists outside this sphere, the model assumes 0% quenching efficiency.

An appropriate formulation of the Perrin model in terms of the sensitized acceptor emission is given by [8]

$$\ln(1 - I/I_\infty)^{-1} = NVC_A, \quad (2)$$

where N is Avogadro's number, V is the volume of the quenching sphere, I is the intensity of acceptor emission at acceptor concentration C_A and I_∞ is the limiting intensity of acceptor emission at “infinite” concentration of A.

We may also handle our data in terms of a simple exciton hopping model in which competitive trapping of the excitons by intrinsic polymer traps and additives is considered [14]. Let ϕ_{tr} be the energy transfer efficiency for the PVCA \rightarrow acceptor system, and assume that the rate of production of the acetone triplet, the energy transfer efficiency of $^3K \rightarrow$ PVCA and the efficiency of acceptor phosphorescence are constant throughout the measurement. Under these conditions, ϕ_{tr} is given by

$$\phi_{tr} = k_h C_A / (k_d + k_h C_A + k_h C_E), \quad (3)$$

where k_h is the rate constant for hopping of triplet excitons, k_d is the inherent rate of deactivation of the triplet polymer, and C_E is the concentration of trapping (excimer forming) sites per mole of basic unit of the polymer. Note that ϕ_{tr} is simply the ratio between the rate of energy transfer to acceptor molecules and the rate of total deactivation of triplets by all pathways, and that $k_h C_E$ is the rate energy transfer to excimer forming sites.

The ratio k_h/k_d is equal to n , the number of exciton jumps in a hypothetical *trap free* polymer

$$\phi_{tr} = \frac{nC_A}{1 + n(C_A + C_E)} = \frac{C_A}{C_A + C_E}. \quad (4)$$

It has been concluded from low temperature phosphorescence measurements and from room temperature fluorescence spectra of PVCA, that efficient ener-

gy transfer to excimer forming sites occurs, so that at sufficiently high concentrations $C_E k_h / k_d \gg 1$. Thus, eq. (3) can be further simplified, as indicated in eq. (4).

4. Discussion

Evaluation of the data relating acceptor chemiluminescence intensity to acceptor concentration according to the Perrin model [eq. (2)] is possible for concentrations lower than 6×10^{-3} M. It is important to note that *both* acceptors DBN and PHTH yield the *same* slope within experimental error. This result is an evidence that energy transfer processes are inherent to the polymer system and do not depend on the acceptor. The slope corresponds to a Perrin volume of 4.0×10^{-19} cm³ and a quenching radius of 46 Å. A quenching radius of this magnitude is, however, very unlikely for single step triplet transfer, typical values for this process being 10 to 15 Å.

The best fit curve to the data in terms of eq. (4) is given by the dashed line in fig. 2. It is apparent that the experimental values indicate a slightly steeper increase of transfer efficiency versus acceptor concentration than expected according to eq. (4).

From the data, an effective concentration of triplet excimer sites is estimated to be $\approx 3 \times 10^{-4}$ mole/mole basic unit. Since this value is considerably lower than that ($\approx 5 \times 10^{-3}$ mole/mole basic unit) estimated at 77 K for triplet excimer sites [5], we conclude that thermal detrapping of weakly bound triplet excimers occurs near room temperature.

Until excimer phosphorescence has been detected near room temperature, the alternative possibility of triplet exciton quenching by some other nonphosphorescent trap cannot be ruled out. The range of triplet excitons is estimated to be about $l = 370$ Å. This value is obtained as end-to-end distance of a random walk with $n = 1/C_E$ jumps and $a = 6.47$ Å (distance between nearest neighbor carbazole groups) according to $l = an^{1/2}$ [18].

5. Conclusions

The results described in this work demonstrate the active participation of triplet exciton migration in PVCA. The appropriate selection of acceptors in combination with chemiluminescence methods to study

the energy transfer process, allow unequivocal and convenient investigation of triplet-triplet transfer.

Acknowledgement

The authors at Columbia University wish to thank the Air Force Office of Scientific Research (Grant AFOSR-74-2589) and the National Science Foundation (Grant NSF-CHE76-18590 and NSF-CHE73-04672) for their generous support of this work. Y.N. wishes to acknowledge the generous financial support from a Fuji Photo Film Overseas Study Grant.

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