Triplet–Triplet Annihilation and Excimer Fluorescence in Poly(naphthyl methacrylate)

A. C. Somersall and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Canada.
Received July 20, 1972

ABSTRACT: The delayed emission spectrum of poly(naphthyl methacrylate) was measured in H_4furan–ether glass at 77°K. The band with peaks at 495, 528, and 550 nm corresponds to the normal phosphorescence of naphthalene and has a mean lifetime of 0.7 sec. The emission at 340 nm has a mean lifetime of 0.1 sec and corresponds to the fluorescence of the naphthalene chromophore. Both the position and lifetime is consistent with a delayed fluorescence (DF) emission similar to that previously observed for poly(1-vinylnaphthalene). The DF intensity was shown to depend on the square of the intensity of excitation which is consistent with a bimolecular triplet–triplet annihilation process for delayed fluorescence. Further evidence for triplet energy migration along the polymer chain has been derived from triplet quenching with piperylene and 1,3-cyclooctadiene. Fluorescence spectra and quenching studies at room temperature also suggest the existence of singlet energy migration leading to excimer formation by coupling of non-nearest-neighbor groups on the random coil in solution.

Intramolecular transfer of excitation energy along a polymer chain is a phenomenon of increasing interest and intensive study. Functional groups situated at regular intervals along the backbone of a polymer molecule may be compared in principle to a one-dimensional crystal and there is a possibility of energy migration from group to group along the chain. This type of energy transfer has been shown to be a common process in molecular crystals and more recently for polymers having aromatic side groups. The chromophores are brought into the necessary orientation in different polymer conformations by a rotation of chain segments, thus facilitating transfer by some energy transfer mechanism. Singlet energy migration has been inferred from studies of excimer fluorescence of polymers including polystyrene, poly(1-vinylnaphthalene),[1] poly(vinyltoluene),[2] and poly(*N*-vinylcarbazole).[3,4]

If ΔW is the energy of interaction between the chromophores, then in an ideal case the uncertainty principle will predict a lifetime $\Delta\tau$ of a chromophore excitation against migration to a new chromophore of the order $h/\Delta W$. Calculations[5] suggest that triplet exciton splittings are smaller than singlet exciton splittings which makes the triplet hopping frequency about a factor of 10^1 to 10^2 less. However the spin forbiddenness of the $T \rightarrow S_0$ transition makes the natural lifetime of the triplet state a factor of 10^6–10^8 longer so that the net triplet transfer should still be much more efficient than singlet transfer in polymer systems. Triplet energy migration has been observed in the phosphorescence quenching of poly(vinylphthalimide),[6] poly(1-vinylnaphthalene,)[7] poly(vinylbenzophenone),[8] poly(phenyl vinyl ketone),[9] and for some of their copolymers with styrene and methyl methacrylate. For such triplet quenching in rigid solution matrices or films at low temperature, intramolecular transfer increases the effective critical radius within which the acceptor molecule is sensitized. Triplet migration has also been demonstrated by the high quenching effect of suitable acceptors on the chemical degradation of polymers, particularly when the acceptor is incorporated in the polymer chain.

Poly(1-vinylnaphthalene), PVN, has been shown[7,10] to exhibit a delayed fluorescence due to triplet–triplet annihilation following intramolecular triplet energy migration through the naphthalene groups. The process is shown schematically in Figure 1 and may be compared to the intermolecular annihilation process which was first observed in rigid solutions of naphthalene by Czarnecki,[11] and the mechanism of which was first demonstrated in fluid solutions of pyrene by Parker and Hatchard.[12] The scheme involves the absorption of two photons by two similar chromophores on the same molecule, forming excited singlet states which intersystem cross to the triplet manifold. The triplet excitation energy migrates (either as a delocalized wave or by a series of hopping events) along the polymer chain by way of the naphthalene rings until two triplets come close enough to undergo annihilation with the formation of a ground singlet and an excited singlet which then fluoresces. The lifetime (τ_{DF}) of the fluorescence emission which results from these successive processes is therefore considerably longer than the normal prompt fluorescence. However, the simple relationship $\tau_{DF} = 2\tau_p$ (the phosphorescence lifetime), which holds in diffusion-controlled systems, does not apply here.[7]

The triplet energy migration has been shown to be intramolecular for PVN[7] since the triplet quenching by piperylene depends on the number of chains in solution and not on the number of monomeric chromophore units. Also, the ratio of delayed fluorescence to phosphorescence in different copolymer compositions with methyl methacrylate drops very markedly when the average mole per cent of vinylnaphthalene units is less than about 30%. These observations have been explained by energy migration along the polymer chain. More recently, David *et al.*[13] compared migration in PVN and polyacenaphthylene. These authors suggested that the similar transfer efficiency and lifetime ($^3\tau$) of both polymers, despite their obvious differences in chromophore configuration, implies that random energy transfer between non-neighboring groups inside the polymer coil could be a better explanation. In this work we have reexamined the question by

(1) M. T. Vala, J. Haebig, and S. A. Rice, *J. Chem. Phys.*, **43**, 886 (1965).
(2) R. C. Powell, *J. Chem. Phys.*, **55**, 1871 (1971).
(3) W. Klopffer, *J. Chem. Phys.*, **50**, 2337 (1969).
(4) P. C. Johnson and H. W. Offen, *J. Chem. Phys.*, **55**, 2945 (1971).
(5) M. T. Vala, J. Haebig, S. A. Rice, and J. Jortner, *J. Chem. Phys.*, **41**, 2846 (1964).
(6) A. I. Lashkov and V. L. Ermolaev, *Opt. Spektrosk.*, **22**, 462 (1967).
(7) R. F. Cozzens and R. B. Fox, *J. Chem. Phys.*, **50**, 1532 (1969).
(8) C. David, W. Demarteau, and G. Geuskens, *Eur. Polym. J.*, **6**, 537 (1970).
(9) C. David, W. Demarteau, and G. Geuskens, *Eur. Polym. J.*, **6**, 1405 (1970).
(10) C. David, W. Demarteau, and G. Geuskens, *Eur. Polym. J.*, **6**, 1397 (1970).
(11) S. Czarnecki, *Bull. Acad. Pol. Sci., Ser. Sci. Chem.*, **9**, 561 (1961).
(12) C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, **59**, 284 (1963).
(13) C. David, M. Lempereur, and G. Geuskens, *Eur. Polym. J.*, **8**, 417 (1972).

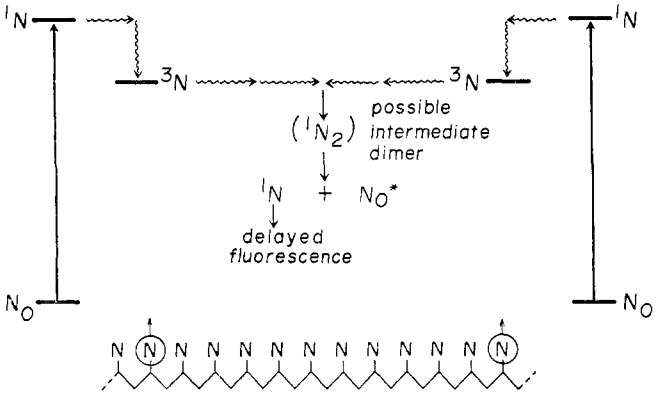

Figure 1. Triplet-triplet annihilation scheme (after Parker and Hatchard).

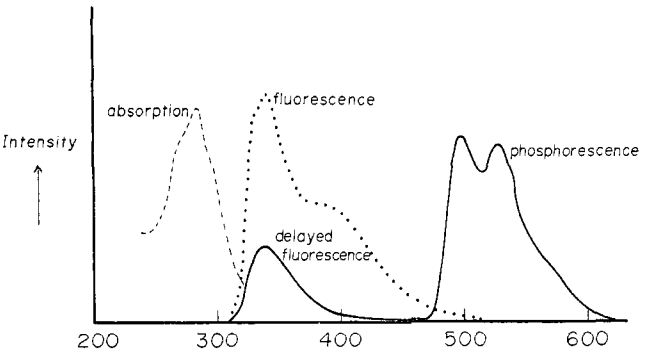

Figure 2. Ultraviolet absorption and emission spectra of poly(naphthyl methacrylate). Dashed line, absorption in chloroform at 25°; dotted line, fluorescence in chloroform at 25°; solid line, delayed emission in H_4furan–ether at 77°K.

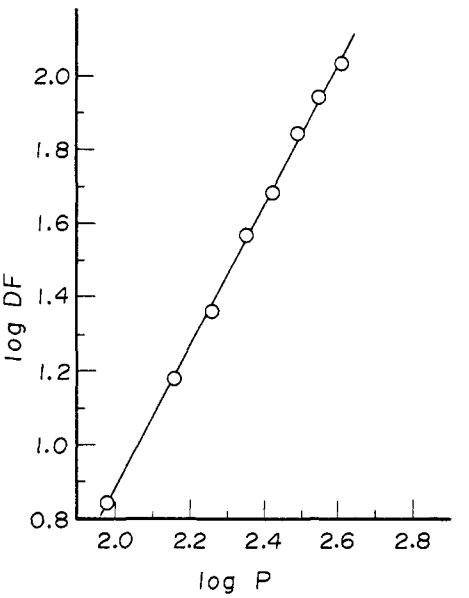

Figure 3. Relation between delayed fluorescence (DF) and phosphorescence (P) of PNMA at various excitation slit widths (T = 77K°).

investigating energy transfer in a third naphthalene polymer system, poly(naphthyl methacrylate) (PNMA).

Excimer fluorescence is a common phenomenon for concentrated solutions of many aromatic hydrocarbons.[14] In recent years similar emission has been characterized for aromatic polymers in films and in solution. We also report here some preliminary studies of the excimer fluorescence of PNMA in different solvents which provide some new insight into the mechanism of excimer formation in polymers in solution.

Experimental Section

Naphthyl methacrylate monomer was synthesized by the Schotten–Baumann reaction of methacrylyl chloride with sodium naphthylate. The monomer was extracted, washed, dried, and redistilled a few times under vacuum. The polymer samples were obtained by free radical polymerization with peroxide in bulk or in toluene solution at 60°, and as a spontaneous product formed in the refrigerator. The polymers were reprecipitated two to three times from methanol and dried in a vacuum oven. The nmr spectra of the polymers showed signals for the naphthalene protons (τ 2–3), for the methyl protons (τ 8–8.8), and for the methylene protons (τ 7–9). The resolution did not allow the estimation of tacticity. The uv spectra of monomer and polymers were virtually indistinguishable in the region of naphthalene absorption. No absorption in the region of the C=C stretching frequency was observed indicating no appreciable traces of monomer.

Tetrahydrofuran and ether were distilled from $LiAlH_4$ and sodium, respectively. 1,3-Cyclooctadiene was distilled on a preparative gas chromatograph, biacetyl was freshly distilled, and piperylene was used as received from Baker Chemical Co. Other solvents were spectroscopic grade. Naphthalene was of "Ultrex" quality from Baker.

Spectra were recorded on a Perkin-Elmer Hitachi MPF-2A fluorescence spectrophotometer fitted with a phosphorescence accessory including a chopper to eliminate prompt signals to the photomultiplier. Solutions 10^{-2} M in naphthalene groups formed clear glasses in 1:1 H_4furan–ether at 77°K. Phosphorescence cells were 2-mm quartz tubes which fitted into a liquid nitrogen dewar whereas fluorescence measurements were obtained in 10-mm quartz cells at room temperature. Relative emission intensities were obtained from relative areas of right angle, ratio-recorded band spectra. Phosphorescence lifetimes were measured from decay curves on an oscilloscope.

Results and Discussion

The ultraviolet absorption spectrum of PNMA in dilute solution in chloroform at 25° is shown in Figure 2 and is similar to the spectra of the small model chromophores, naphthalene or ethylnaphthalene. The assignment of the spectrum to weakly interacting, independently absorbing naphthalene groups in the ground state is therefore certainly reasonable. However, the emission spectra provide definitive evidence for the importance of chromophore interactions involving excited states.

Delayed Emission Spectra at 77°K. The delayed emission spectrum of PNMA at 313 nm excitation (Figure 2) shows two distinct bands. The peaks at 495 and 528 nm and a shoulder at 550 nm correspond to the normal phosphorescence of naphthalene or 1-ethylnaphthalene and have a mean lifetime of 0.7 sec. The emission at 340 nm has a mean lifetime of 0.1 sec and corresponds to the fluorescence peak of the naphthalene chromophore. Both the position and lifetime of this band are consistent with a delayed fluorescence emission similar to that observed for poly(1-vinylnaphthalene).[7] A log–log plot of the area under the fluorescence and phosphorescence peaks (Figure 3) was obtained by varying the excitation slit width over a spectral band width of 1–20 nm. The slope of the straight line is 2.0 ± 0.1 which is completely consistent with a bimolecular triplet–triplet annihilation process for delayed fluorescence.

As has been pointed out for PVN, chains of PNMA fix the naphthalene chromophores closely to each other in space and permit the contact usually necessary for triplet transfer. Molecular motion is negligible in the low-temperature glasses used for delayed emission spectra. Triplet transfer therefore takes place under these static conditions. Two alternative static T–T interaction mechanisms

(14) For a review, see J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, London, 1970.

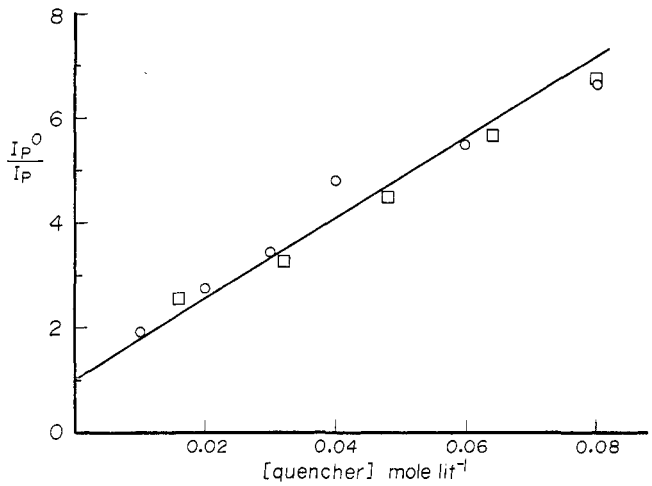

Figure 4. Quenching of PNMA phosphorescence: (○) piperylene; (□) 1,3-COD.

have been proposed:[14] Parker[15] suggested a scheme involving dipole–dipole energy migration to a higher triplet state followed by intersystem crossing to the first singlet excited state. Naqvi[16] has pointed out the inadequacy of this scheme and has proposed a more plausible mechanism, not involving molecular diffusion or rotation. The triplet energy migrates by electron-exchange interaction over distances up to ~15 Å to sites at which two triplets can interact by another electron exchange-interaction process

$$\text{migration} \quad {}^3N + N_0 \longrightarrow N_0 + {}^3N \qquad (1)$$

$$\text{annihilation} \quad {}^3N + {}^3N \longrightarrow {}^1N + N_0 \qquad (2)$$

Many observations in rigid solutions have confirmed the Naqvi mechanism for small molecules and all the results on the polymers are consistent with the same scheme with the addition of *intra*molecular triplet migration among the naphthalene chromophores.

Cozzens and Fox[7] reported that similar delayed emission spectra for PVN resulted from both direct excitation at 290 nm and excitation of a mixture of PVN and benzophenone at 366 nm, where PVN does not absorb. Triplet sensitization of PVN by benzophenone (and hence direct population of the triplet state of PVN followed by annihilation and delayed fluorescence in the polymer) was considered to be further evidence for the annihilation mechanism. However, our attempts to sensitize annihilation in PNMA directly through triplet–triplet transfer from benzophenone with sensitizer concentrations up to 0.05 *M*, resulted in delayed emission spectra at 366-nm excitation which showed only phosphorescence of benzophenone and naphthalene chromophores. The failure to observe delayed fluorescence in this way is consistent with the more recent observations of David *et al.*[10] which suggest that benzophenone is an exothermic singlet quencher of the excited singlet state of PVN. We suggest that any singlets formed by annihilation in PNMA in the presence of benzophenone are probably quenched effectively by the benzophenone so that no delayed fluorescence is observed in this case. Direct observation of the quenching of the prompt fluorescence from the PNMA singlet by benzophenone was not feasible because the absorption coefficients of PNMA and benzophenone are similar in the region of excitation of PNMA fluorescence. Furthermore, the inner filter effect due to the reabsorption of the naphthalene fluorescence by benzophenone would make any direct quenching results ambiguous.

Table I
Delayed Luminescence Quenching Data for Naphthalene Polymers

Donor	Quencher	Emission	Plot	Slope M^{-1}
PNMA	1,3-COD	Phosphorescence	Stern-Volmer	76
PNMA	Piperylene	Phosphorescence	Stern-Volmer	76
PVN	Piperylene	Phosphorescence	Stern-Volmer	42[a]
PAcN	Piperylene	Phosphorescence	Stern-Volmer	50[b]
PNMA	1,3-COD	Delayed fluorescence	Perrin	70
PNMA	Piperylene	Delayed fluorescence	Perrin	26

[a] Calculated from R. F. Cozzens and R. B. Fox, *J. Chem. Phys.*, **50**, 1532 (1969). [b] Results of C. David, M. Lempereur, and G. Geuskens, *Eur. Polym. J.*, 8, 417 (1972).

Phosphorescence Quenching at 77°K. Further evidence for triplet energy migration along the polymer chain has been derived from triplet quenching with piperylene and 1,3-cyclooctadiene (COD). Both quenchers have negligible absorbance in the region of excitation (310 nm); neither quenches the phosphorescence of 1-ethylnaphthalene or naphthalene. However, on addition of these triplet quenchers to solutions of PNMA, both the phosphorescence and delayed fluorescence intensities are reduced. The phosphorescence quenching is well described by the Stern-Volmer model defined by the equation

$$\frac{I^0}{I} = 1 + k_q\tau[Q] \qquad (3)$$

where I^0 is the emission intensity in the absence of quencher, I is the intensity at quencher concentration [Q], τ is the excited state lifetime and k_q is the quenching rate constant which is usually similar to k_{diff}, the diffusion rate constant. Stern-Volmer plots of the phosphorescence quenching are shown in Figure 4. The slopes of the straight lines are similar for both quenchers, and are almost a factor of two higher than the slope for piperylene quenching of PVN phosphorescence reported by Cozzens and Fox (Table I).[7] The Stern-Volmer kinetics observed suggest that in the case of triplet transfer with annihilation, a dynamic process involving migration or diffusion is a more appropriate model, in contrast to the static Perrin model observed for phosphorescence quenching of small molecules.[17] The Perrin model would predict a logarithmic dependence of phosphorescence intensity with change in quencher concentration. The Stern-Volmer plots for polymer phosphorescence quenching afford estimates of a bimolecular quenching constant, k_Q, which may be associated with the product of the triplet lifetime ($^3\tau$) and a triplet energy migration constant (k_t). The migration is analogous to a triplet exciton diffusion among the naphthalene chromophores in a matrix. Material diffusion of the quencher is negligible under these conditions. David *et al.*[8,13] applied the theory developed by Voltz *et al.*[18] to the results for PVB, PVN, and PAcN. We applied the same treatment to our results on PNMA, as follows:

$$k_Q = k_t{}^3\tau \text{ l. mol}^{-1} \qquad (4)$$

$$k_t = 4\pi N_0 \lambda R_0 \times 10^{-3} \text{ l. mol}^{-1} \text{ sec}^{-1} \qquad (5)$$

where k_Q is 75 l. mol^{-1} and $^3\tau$ is 0.7 sec for PNMA, N_0 is Avogadro's number, λ is the migration coefficient, and R_0 is the critical transfer distance between donor and accep-

(15) C. A. Parker, "The Triplet State," Cambridge University Press, Cambridge, 1967, p 353.
(16) K. R. Naqvi, *Chem. Phys. Lett.*, 1, 497 (1968).
(17) V. L. Ermolaev, *Sov. Phys. Dokl.* 6, 600 (1962).
(18) R. Voltz, A. Laustriat, and A. Coche, *J. Chim. Phys.*, 63, 1253 (1966).

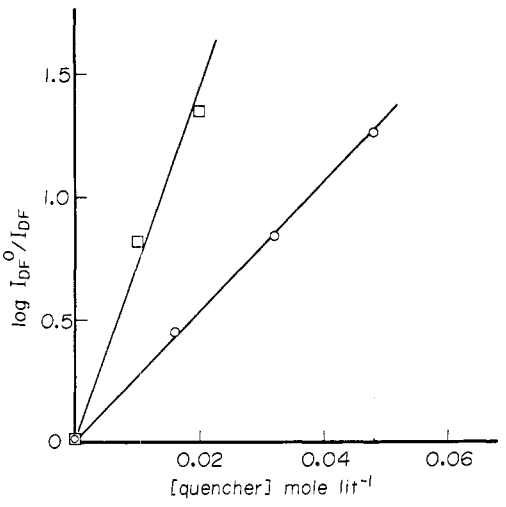

Figure 5. Quenching of PNMA delayed fluorescence: (□) piperylene; (○) 1,3-COD.

tor for which the transfer probability $p = 1$ if $R \leq R_0$ and $p = 0$ if $R > R_0$. If R_0 is assumed to be 11 Å,[17] then the migration coefficient $\lambda = 1.3 \times 10^{-13}$ cm^2 sec^{-1}. From elementary diffusion theory

$$\omega = \frac{6\lambda}{\bar{r}^2} \tag{6}$$

where $\bar{r}^2$ is the rms displacement of excitation in time $1/\omega$. Assuming that $\bar{r} = 5$ Å, the mean distance between naphthalene groups,[13] then $\omega = 300$ sec^{-1} in PNMA. David *et al.* obtained $\omega = 128$ sec^{-1} for PVN and PAcN in glassy solutions and $\omega = 7 \times 10^4$ sec^{-1} for PVB films. The similarity of k_Q values observed for PAcN and PVN led David *et al.* to suggest energy may be random between nonneighboring groups inside the polymer coil. The higher k_Q value we obtained for PNMA with two different quenchers and the shorter lifetime for phosphorescence decay measured both seem to show that triplet migration is more efficient in the case of PNMA. This may be due to steric or conformational effects which provide better overlap of chromophores in the polymethacrylate with its more bulky side groups, or may be due to factors involving the nature of the low temperature matrix in which the measurements are made. The question of random migration in contrast to more ordered transfer along the chain or within the polymer coil remains open.

Delayed Fluorescence Quenching at 77°K. In contrast to phosphorescence, the quenching of the delayed fluorescence with COD and piperylene (Figure 5) shows a logarithmic dependence on quencher concentration consistent with the more static Perrin model, defined by

$$\frac{I^0}{I} = e^{-vN'[Q]} \tag{7}$$

where v is the volume of the sphere about the quencher molecule within which any excited chromophore is inevitably quenched and N' is the number of molecules per milliliter in a 1 M solution. Direct observation of the quenching of normal naphthalene and PNMA fluorescence by piperylene in room temperature solutions shows that it is an inefficient quencher of the singlet excited state. From the Stern-Volmer slope for quenching of naphthalene in aerated cyclohexane we obtained a quenching rate of 2×10^8 compared to the diffusion rate of order 10^{10}. COD is an even more inefficient quencher of naphthalene and PNMA fluorescence and also is less efficient in quenching delayed fluorescence in the polymer (PNMA) than is piperylene (Figure 5). The kinetics would not be consistent with delayed fluorescence quenching due primarily to the quenching of the triplets before they annihilate. The mutual diffusion of two triplets is faster than the diffusion of a triplet to the immobile quencher and the annihilation event is itself very fast.[19] The rate of formation of excited singlets by annihilation could therefore be independent of quencher concentration. If this is so, the delayed fluorescence quenching would be expected to follow normal Perrin kinetics.

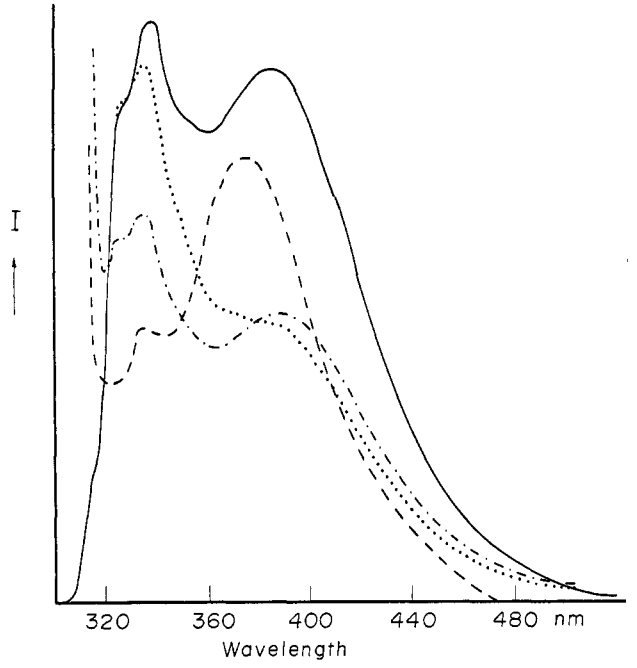

Figure 6. Fluorescence of PNMA in different solvents (25°). The intensities of the total spectra are not comparative for the different solvents but each spectrum shows the ratio of "monomer" to "excimer" fluorescence. In EtOAc and the $CHCl_3$-cC_6H_{12} mixture, the recorder signal is further attenuated by a factor 3. (——) In benzene; (- - -) in EtOAc; (·····) in chloroform; (·-·-·) in chloroform-cyclohexane (1:1).

The alternative possibility of quenching the delayed fluorescence by quenching the triplets before they annihilate would predict a square dependence and is inconsistent with the observations. From the Perrin plots, one can estimate the critical Terenin sphere about the quencher molecule within which intermolecular transfer must take place. The radii of these spheres are thus estimated to be 30 and 40 Å for piperylene and COD quenching, respectively. These large values may define critical spheres within which two excited triplets do invariably annihilate to form an excited singlet which is inevitably quenched. The measurements made do not provide any indication as to whether these singlets formed by annihilation migrate under these conditions. The absence of delayed excimer fluorescence is not definitive since excimer fluorescence yields are relatively low in any case. The lifetime measured for delayed fluorescence decay (0.1 sec) is much longer than the actual lifetime of the excited singlet state formed by annihilation. The short lifetime of this state may be an important factor preventing singlet transfer under these immobile conditions.

Fluorescence Spectra at 25°. Fluorescence spectra of PNMA at room temperature contain two main bands, a simple mirror image of the absorption band and a broad, structureless band shifted toward longer wavelengths (375-390 nm) (Figure 6). In ethyl acetate, the band at 380 nm was predominant, in benzene it was just resolved as a

(19) V. A. Krishna, *J. Chem. Phys.*, 46, 1735 (1967).

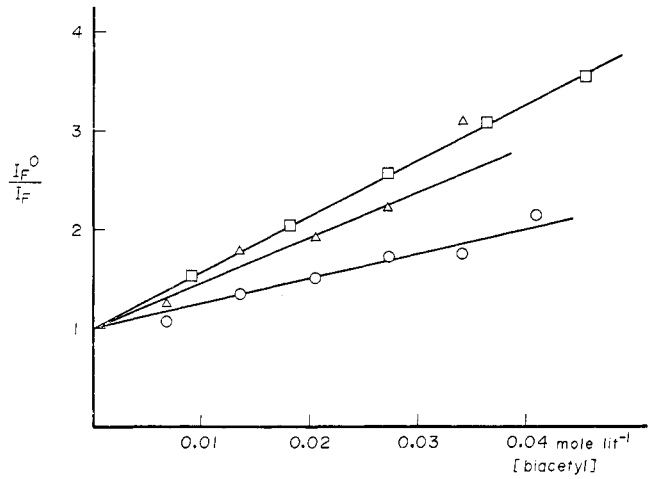

Figure 7. Fluorescence quenching of naphthalene and PNMA by biacetyl in chloroform at 25°: (□) naphthalene; (○) PNMA total fluorescence emission; (△) PNMA excimer fluorescence only.

broad peak beside the fluorescence at 340 nm and in chloroform the anomalous band appears as a very broad shoulder. Bairamov, Amerik, and Krensel[20] observed a similar broad peak at 385 nm in dioxane solution and showed that in copolymers of NMA and MMA the intensity of this band decreased with increase in MMA content. As these authors have suggested, interaction of adjacent side groups in the ground state is unlikely because the absorption spectra of homopolymers, copolymers, and model monomers are similar. Similar observations have been made for polystyrene, PVN,[1] poly(vinyltoluene),[2] PAcN,[13,21] and poly(*N*-vinylcarbazole).[3,4] The anomalous emission at longer wavelengths has been attributed to the emission of an excimer formed by the interaction of an excited chromophore with a nearby chromophore on the same polymer chain. The assignment to an excimer emission is consistent with the following observations: (1) the band is broad and structureless; (2) the emission maximum is red shifted by about 5000 cm^{-1} which is typical for aromatic hydrocarbons; and (3) the long-wavelength band is quenched by oxygen to a greater extent than the shorter wavelength band. Migration of singlet excitons to a pair of chromophores which are in the necessary spatial conformation for excimer formation has therefore been suggested to take place in these polymers.[1-4,10] Detailed information about the conformational changes required for excimer formation, the number of such sites, and the location of the coupled chromophores along the chain is still generally lacking.[4]

In a poor solvent such as ethyl acetate, the excimer band is predominant and much more intense, whereas in a better solvent such as chloroform it is not quite resolved and appears as a broad shoulder. When cyclohexane (a nonsolvent) was added to a solution of the polymer in chloroform in 1:1 ratio (just before the cloud point), the excimer emission was again very intense as in the poor solvent ethyl acetate. Benzene is an intermediate case where both the normal fluorescence and the excimer band are clearly observed (Figure 6). These observations suggest that for PNMA the coupled chromophores in the excimer are non-nearest neighbors which are brought into contact by the chain folding back on itself. They also imply that excimer emission may serve as a probe for conformational changes in solution.

This type of non-nearest-neighbor coupling is also necessary for the excimer fluorescence of polyacenaphthylene previously observed and confirmed by us, since nearest-neighbor interaction is impossible in this case. However, Fox *et al.*[21] observed no solvent effects in the excimer emission of PVN which is consistent with nearest-neighbor coupling for that polymer. Space-filling models suggest that the naphthalene groups in PVN like the benzene rings in PS and PVT can stack in sandwich-like conformations without much difficulty. On the other hand, similar models of PNMA show that adjacent naphthalene groups form sandwich-like conformations only with great difficulty, if indeed they do so at all. Such conformations are therefore more probably formed in dilute solution by the approach of distant chromophores on the same chain, brought together by folding of the polymer backbone. The analysis of the (p,T) dependence of excimer emission from poly(*N*-vinylcarbazole) films[4] has given evidence for non-nearest-neighbor interaction in this system also where the side groups are bulky and the flexibility of the polymer chain is greatly restricted. It is also not unlikely that the T-T annihilation scheme may result from the coupling of non-nearest-neighbor triplet naphthalene groups, frozen out in some suitable conformation at liquid nitrogen temperatures. These excimer sites then serve as traps for the migrating excitons in a manner analogous to molecular crystals.

Table II
Quenching Rate Constants (k_Q) Values for Fluorescence Quenching with Biacetyl at 25° (l. mol^{-1} sec^{-1})

	Total Fluorescence			Excimer Only
Solvent	Naphthalene	PNMA	PVN	PNMA
Benzene	235	36	118	58
Chloroform	57	28		52
Ethyl acetate	167		77	58

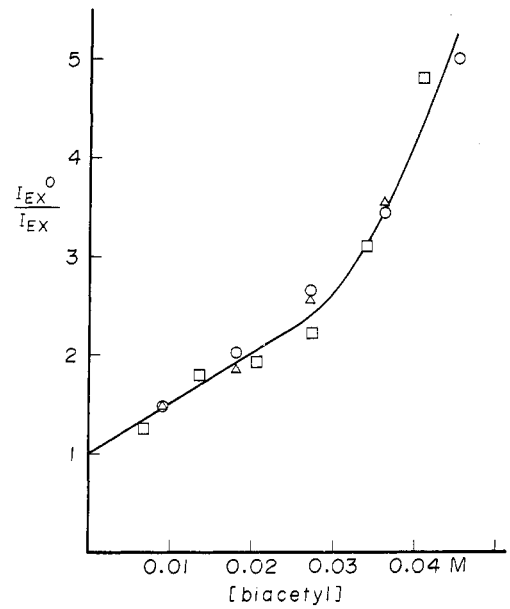

Figure 8. Excimer fluorescence quenching by biacetyl at 25°: (○) in benzene; (□) in chloroform; (△) in EtOAc.

Fluorescence Quenching. Figure 7 shows the Stern-Volmer plots for the fluorescence quenching of naphthalene and PNMA by biacetyl in chloroform. Similar plots have been obtained for PVN and in different solvents. The quenching constants are tabulated in Table II. The k_Q

(20) Y. Y. Bairamov, Y. B. Amerik, and B. A. Krensel, Presented at the 3rd IUPAC International Conference, Bratislava, June 1971, Preprint III.

(21) R. B. Fox, T. R. Price, R. F. Cozzens, and J. R. McDonald, *J. Chem. Phys.*, in press.

(*i.e.*, $k_q\tau$) values for the quenching of fluorescence in the polymers are about half the value for naphthalene. In previous studies[22] Heskins and Guillet demonstrated that for these systems polymer diffusion may be neglected. Thus, if the singlet lifetimes of the chromophores were similar, the k_Q values would suggest that the efficiency of singlet quenching is not significantly different for isolated and adjacent naphthalene groups. However, the quenching of the PNMA excimer band alone shows a higher quenching efficiency and a marked curve upwards with increasing quencher concentration (Figure 8). This curvature suggests that intermolecular quenching competes effectively with excimer formation by singlet migration in the polymer at sufficiently high quencher concentration. The kinetic scheme is described by

$$N \xrightarrow{h\nu} N^* \quad (8)$$

$$N^* \longrightarrow N + h\nu_f \quad (9)$$

$$\longrightarrow N \quad (10)$$

$$\longrightarrow {}^3N \quad (11)$$

$$\xrightarrow{(N)} E^* \text{ (excimer)} \quad (12)$$

$$E^* \longrightarrow N^* + N \quad (13)$$

$$\longrightarrow N + N + h\nu_{ex} \quad (14)$$

$$\longrightarrow N + N \quad (15)$$

In the presence of added quencher

$$N^* + Q \xrightarrow{k_{qN}} N + Q^* \quad (16)$$

$$E^* + Q \xrightarrow{k_{qE}} N + N + Q^* \quad (17)$$

It can be shown that the ratio of the excimer fluorescence intensity in the absence and presence of the quencher at concentration [Q] is given by

$$\frac{I_{Ef}^0}{I_{Ef}} = \frac{\phi_{Ef}^0}{\phi_{Ef}} = 1 + \left[\left(\frac{k_{qE}}{\tau_N} + \frac{k_{qN}}{\tau_E}\right)[Q] + k_{qE}k_{qN}[Q]^2\right]\tau_N\tau_E \quad (18)$$

where τ_N and τ_E are lifetimes of the chromophore and excimer singlet states. The first term in [Q] in eq 18 accounts for the higher quenching efficiency in the linear portion of the plot in Figure 8. The curvature at higher values of [Q] shows the importance of the second term in $[Q]^2$.

Conclusions

Strong evidence has been observed for the process of triplet–triplet annihilation in PNMA in H_4furan–ether glasses at 77°K, leading to delayed fluorescence emission from the polymer. Intermolecular quenching of the emission from the polymer under these conditions shows very efficient triplet migration among the chromophores on the polymer chain by a mechanism similar to a diffusion process. The delayed fluorescence quenching is well described by the static Perrin model in the low-temperature glasses. Fluorescence spectra including excimer emission and quenching in room-temperature solutions show that intramolecular singlet migration does take place under these more mobile and flexible conditions. Solvent effects in the excimer emission do suggest that the coupled chromophores which form the excimer are non-nearest neighbors. Excimer emission may therefore be a useful probe of the conformation of aromatic polymers in solution.

Acknowledgments. The authors thank the National Research Council of Canada and Imperial Oil Enterprises Limited for their generous financial support of this research.

(22) M. Heskins and J. E. Guillet, *Macromolecules*, 3, 224 (1970).

Studies of Diffusion in Polymers by Gas Chromatography

D. G. Gray† and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto 181, Canada. *Received August 23, 1972*

ABSTRACT: The shapes of eluted peaks in gas chromatography on polymeric substrates are governed by several factors, one of the most important being slow diffusion in the polymer phase. By a suitable choice of conditions, the simple Van Deemter equation enables diffusion coefficients to be calculated from the variation in chromatographic peak width with carrier gas flow rate. The method is found to be applicable to some hydrocarbon penetrants in a polyethylene stationary phase.

In most previous gas chromatographic investigations of a polymeric stationary phase,[1-4] the primary experimental data were the chromatographic peak retention times for suitable volatile "probe" molecules. The shapes of the chromatographic peaks were of secondary interest. However, peak shape may have a significant effect on the validity of data derived from peak retention measurements, and in addition may be related to the thermodynamics and kinetics of the polymer–probe interaction. In this paper, the factors which govern peak shape in gas chromatography are outlined, and their relevance to diffusion measurements on polymeric substrates is investigated.

Ideally, an infinitely sharp input of vapor into a gas chromatograph should result in an infinitely sharp peak being eluted at the detector after a time interval dependent only on the interaction between the vapor and the stationary phase in the column. In practice, the vapor input is not infinitely sharp, and the eluted peak is broadened and skewed by a wide range of factors. These broadening factors may be divided into three main classes.

†Pulp and Paper Building, Chemistry Department, McGill University, Montreal 101, Canada.

(1) O. Smidsrod and J. E. Guillet, *Macromolecules*, 2, 272 (1969).
(2) J. E. Guillet, *J. Macromol. Sci., Chem.*, 4, 1169 (1970).
(3) D. Patterson, Y. B. Tewari, H. P. Schreiber, and J. E. Guillet, *Macromolecules*, 4, 365 (1971).
(4) W. E. Hammers and C. L. DeLigny, *Recl. Trav. Chim. Pays-Bas*, 90, 912 (1971).