ENERGY TRANSFER IN POLYMERS—II*

SOLID POLYVINYLNAPHTHALENE–BENZOPHENONE SYSTEM AND COPOLYMERS VINYLNAPHTHALENE–VINYLBENZOPHENONE

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Abstract—No luminescence other than excimer fluorescence could be detected for polyvinylnaphthalene. Absence of any normal fluorescence or phosphorescence suggests singlet migration and T.T. annihilation. Singlet energy transfer from solid polyvinylnaphthalene to benzophenone at 77°K is in agreement with Förster theory for dipole–dipole interaction ($R_0 = 15$ Å). In copolymers, transfer efficiency from vinylnaphthalene to vinylbenzophenone units is unity; neither naphthalene nor benzophenone phosphorescence was observed.

MANY processes may contribute to solvent–solute energy transfer.

(1) Trivial radiative process in which the light emitted by the donor is reabsorbed by the acceptor.

(2) Non-radiative process due to coulombic long range (50–100 Å) interaction between donor and acceptor.[1]

(3) Non-radiative process due to short range (10–15 Å) exchange interaction between donor and acceptor.[2,3]

(4) Excitation migration due to short range resonance interaction between neighbouring molecules.[4–6]

(5) Diffusion of excited solvent and solute molecules.[4–6]

The purpose of this work is to analyse the emission spectra and to elucidate the mechanism of energy transfer in solid polymeric systems, (a) polyvinylnaphthalene (PVN), (b) PVN containing benzophenone or anthracene and (c) copolymers vinylnaphthalene–vinylbenzophenone, irradiated at 3660 or 3130 Å at liquid nitrogen or room temperature.

EXPERIMENTAL

Apparatus and techniques for recording the emission spectra were described in Part I.* PVN was obtained by slow polymerization of 1-vinylnaphthalene at room temperature.

The polymer was purified by successive dissolution in benzene and precipitation in methanol. The limiting viscosity number measured in benzene is $0·05$ dl.g^{-1}. Another sample synthesized at 60° in the presence of AIBN gave identical emission spectra.

Copolymerization were initiated by AIBN at 60°. The copolymers were purified by successive dissolution in benzene and precipitation in methanol. Their composition was determined by absorption spectroscopy at 3650 Å in benzene using $\epsilon_{benzophenone} = 96$ l.mole^{-1} cm^{-1}. The ratio of benzophenone to naphthalene units was respectively $2·6$ and $0·3$ for copolymers A and B.

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*Part I: C. David, W. Demarteau and G. Geuskens, *Europ. Polym. J.* **6**, 537 (1970).

RESULTS

Only a broad excimer emission, the maximum of which is situated at 4000 Å is obtained for pure PVN films irradiated at liquid nitrogen temperature (*LNT*) and room temperature (*RT*) at a wavelength of 3130 Å (Fig. 1). The emission intensity was the same at these two temperatures. No emission could be detected by excitation at 3660 Å,
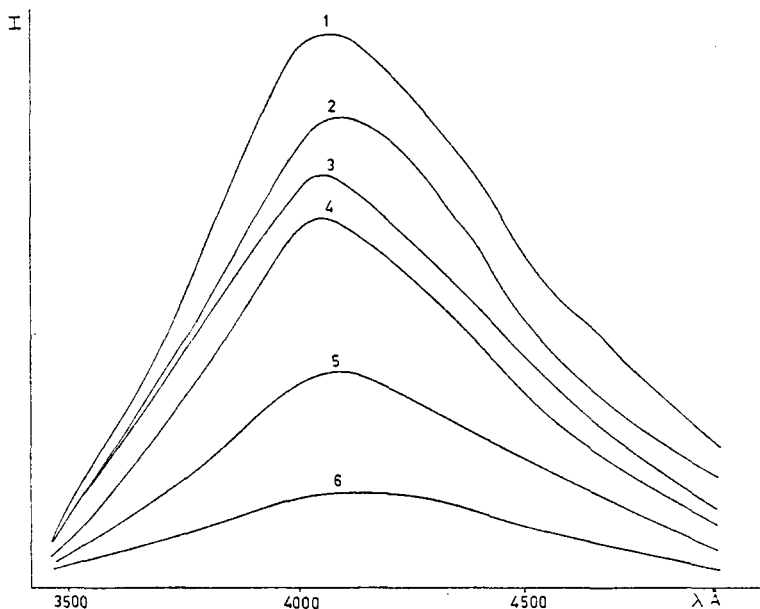

FIG. 1. Emission spectrum of PVN films containing benzophenone excited with $\lambda = 3130$ Å at *LNT*. Mole fraction benzophenone (1) 0 or $2 \cdot 7.10^{-5}$. (2) $2 \cdot 7.10^{-4}$. (3) $1 \cdot 3.10^{-3}$. (4) $2 \cdot 7.10^{-3}$. (5) $1 \cdot 3.10^{-2}$. (6) $2 \cdot 7.10^{-2}$.

TABLE 1

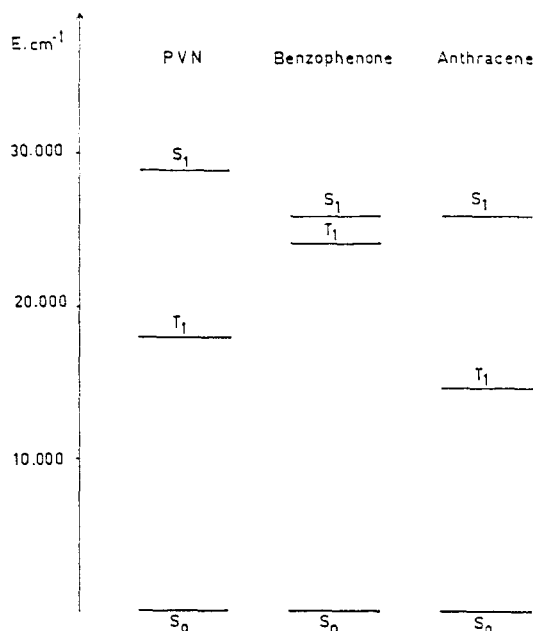| System	Excitation (Å)	Excimer emission	Other emission
PVN	3130	Yes	No
	3660	No	No
Copolymers VN–VB	3130	No	No
	3660	No	No
PVN + benzophenone	3130	Yes decreases with concentration of benzophenone	No
	3660	No	No
PVN + anthracene	3130	Yes decreases with concentration of anthracene	Anthracene fluorescence

FIG. 2. Energy levels diagram for the systems PVN, benzophenone and anthracene.

the absorption of PVN being almost zero at that wavelength. Concerning copolymer films, no fluorescence or phosphorescence could be measured at *LNT* or *RT* in spite of the important absorptions at 3660 and 3130 Å. Films of PVN containing various amounts of benzophenone exhibit, when irradiated at 3130 Å, the same broad emission at 4000 Å as pure PVN films. This decreases with increasing concentration of benzophenone (Fig. 1). No other emission could be detected. When the same films are irradiated at 3660 Å (where benzophenone only absorbs), no luminescence was observed at *LNT* or *RT*. For polymethylmethacrylate films containing benzophenone and irradiated at 3660 Å, normal benzophenone phosphorescence is emitted. With PVN samples containing increasing amounts of anthracene as acceptor, the band at 4000 Å is gradually replaced by the fluorescence of anthracene (Fig. 2). These results are summarized in Table 1.

DISCUSSION

Emission spectrum of pure solid PVN excited to its first singlet state with light of 3130 Å at *RT* or *LNT*, is characterized by the absence of any normal fluorescence and phosphorescence.
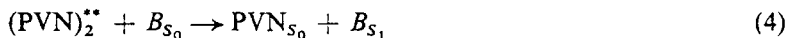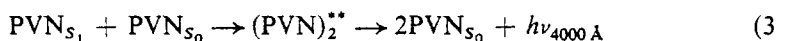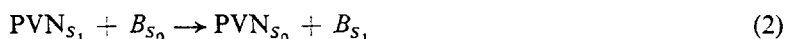
The broad structureless emission around 4000 Å has been observed for the polymer in solution at *RT* and attributed to excimer emission.[7] Excimer fluorescence is frequently emitted in the course of radiative deactivation of aromatic systems and has its origin either in complex formation between excited singlet and unexcited molecule or in triplet deactivation by mutual annihilation:[8]

$$X_{T_1} + X_{T_1} \rightarrow X_2^{**} \; \rightleftharpoons \; X_{S_1} + X_{S_0}$$
$$\downarrow hv', - \uparrow\downarrow + hv$$
$$2X_{S_0} \qquad X_{S_0}$$
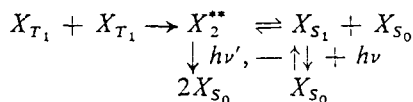
Life-time of the excited state allows discrimination between these two mechanisms. PVN excimer emission life-time was measured to be less than 10^{-3} sec and can thus be assigned to complex formation. The existence of delayed excimer luminescence due to triplet–triplet annihilation in the polymer can however not be excluded since this type of emission usually has a very low intensity and long-lived emission corresponding to 10 per cent or less of the total excimer intensity and could not be detected with our apparatus. Absence of PVN phosphorescence can be assigned to triplet migration and most probably annihilation in the polymer. Such migration and annihilation are in fact thought to be responsible for the lack of phosphorescence in naphthalene crystals.[†][9]

The failure to observe any normal fluorescence at *RT*, as well as at *LNT*, indicates that singlet energy migrates from naphthalene to naphthalene group until the excitation is trapped at a pair of chromophores which have the mutual correct space orientation for excimer formation. It is very improbable indeed that excimer could be formed at the site of photon absorption since this would mean that each naphthalene group has at least one first neighbour satisfying the strict orientation requirements for excimer formation.[7,10]

Examination of energy levels reported in Fig. 2 shows that the most probable mechanism for energy transfer from PVN to benzophenone is:

$$PVN \quad \xrightarrow{3130\,\text{Å}} \quad PVN_{S_1} \tag{1}$$

$$PVN_{S_1} + B_{S_0} \longrightarrow PVN_{S_0} + B_{S_1} \tag{2}$$

$$PVN_{S_1} + PVN_{S_0} \longrightarrow (PVN)_2^{**} \longrightarrow 2PVN_{S_0} + h\nu_{4000\,\text{Å}} \tag{3}$$

$$(PVN)_2^{**} + B_{S_0} \longrightarrow PVN_{S_0} + B_{S_1} \tag{4}$$

$$B_{S_1} \longrightarrow B_{T_1} \tag{5}$$

$$B_{T_1} + PVN_{S_0} \longrightarrow B_{S_0} + PVN_{T_1}. \tag{6}$$

Absence of any naphthalene or benzophenone phosphorescence however requires some comments. Decrease in PVN excimer intensity in the presence of benzophonone suggests that energy transfer occurs although no acceptor emission can be detected.

Transfer from PVN singlet state is demonstrated in another way: when the acceptor is anthracene instead of benzophenone, step 5 does not occur and acceptor fluorescence is observed. It is furthermore very improbable that the polymer matrix modifies the high yield usually observed for step 5 since normal benzophenone phosphorescence is observed in PMMA. The lack of PVN or benzophenone phosphorescence must thus be attributed to T.T. annihilation due to triplet migration in PVN containing benzophenone as in pure PVN.

Films of copolymers vinylnaphthalene–vinylbenzophenone behave qualitatively as a mixture of PVN and the corresponding amount of benzophenone, no emission being observed either from the donor, or from the acceptor.

Transfer efficiency from PVN to benzophenone can be quantitatively characterized. Transfer between singlet states has been widely studied in fluid and glassy media.

†After completion of this work, R. F. Cozzens and R. B. Fox [*J. Chem. Phys.* **50**, 1532 (1969)] reported that PVN in a rigid glass at 77°K exhibits a delayed fluorescence due to T.T. annihilation.

When donor and acceptor remain stationary and no type of energy migration is allowed, coulombic long-range interaction is operative[1] and Förster theory applies. This gives for the quantum yield η_A of the acceptor fluorescence and transfer efficiency f[1]

$$f = \frac{\eta_A}{\eta_A^{max}} = 2x\, e^{x^2} \int_x^\infty e^{-t^2 dt} = \sqrt{x}\, e^{x^2} \left[1 - \phi(x)\right] \tag{7}$$

with $\qquad\qquad x = \frac{\sqrt{\pi}}{2} \frac{c}{c_0} \qquad\qquad \phi(x) = \text{error function}$

and $\qquad\qquad\qquad\qquad\qquad c_0 = \dfrac{3000}{4\pi N R_0^3}.$

Here η_A^{max} is the maximum luminescence yield of the acceptor, c the acceptor concentration and c_0 a parameter called the critical concentration. For $c/c_0 = 1$, $f = 0.72$ and an experimental value of R_0 can be obtained from the experiments. R_0 can also be calculated from measured spectroscopic properties of donor and acceptor:[1]

$$R_0^6 = \frac{9000 (\ln 10)\, K^2}{128\, \pi^5\, n^4\, N_0} \int_0^\infty f_s(\nu)\, \epsilon_s(\nu)\, \frac{d\nu}{\nu^4} \tag{8}$$

where n is the solvent refractive index

K^2 is an orientation factor

$\epsilon_s(\nu)$ is the molar extinction coefficient at wavenumber ν

$f_s(\nu)$ is the relative donor fluorescence quantum intensity at ν normalized by the relation

$$\int_0^\infty f(\nu)\, d\nu = \phi.$$

where ϕ is the donor fluorescence quantum yield.

If $R_{0_{calc.}} \neq R_{0_{exp.}}$ the rate of energy transfer can be interpreted in terms of energy migration and diffusion in the system.[4–6]

Efficiency of transfer, as a function of c for the system PVN–benzophenone, is reported in Fig. 3. A R_0 value of 15 Å was deduced from these experiments. R_0 was
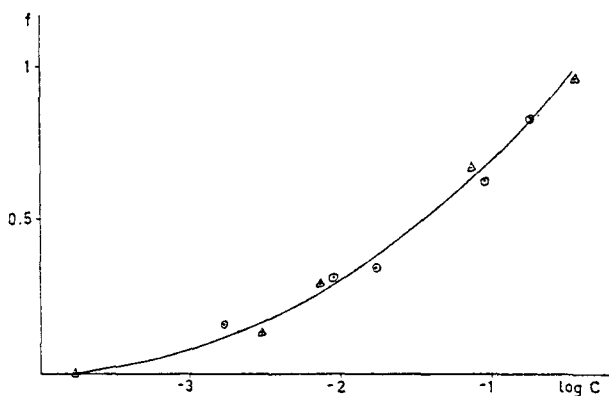

Fig. 3. Transfer efficiency as a function of log benzophenone concentration for the system PVN–benzophenone excited with $\lambda = 3130$ Å at *LNT*. $\triangle$ and $\bigcirc$ correspond to two independent series of experiments.

also calculated from Eqn. (8). A value of 14 Å is found assuming for n and ϕ the most probable values of 1·5 and 0·5.[2] For two sets of extreme values of n and ϕ (respectively 1·2 and 1 or 1·7 and 0·2) R_0 was 17 Å and 11 Å. If transfer occurs from the excimer to benzophenone, the value of the overlap integral in Eqn. (8) is about one tenth that obtained for monomeric singlet assuming that the excimer fluorescence quantum yield is five times lower that the normal fluorescence quantum yield. In this case, the preceding R_0 values are to be multiplied by 0·68.

The agreement between calculated and experimental R_0 indicates that long-range dipole–dipole transfer according to Förster theory is mainly operative in this polyvinylnaphthalene–benzophenone system.

An equation of the Stern–Volmer type is obtained by a formal kinetic treatment:

$$f = \frac{k_t \tau c}{1 + k_t \tau c}$$

where k_t is the rate constant for transfer
   τ is the life-time of the donor in the absence of acceptor
   c is the acceptor concentration.

or in a modified form
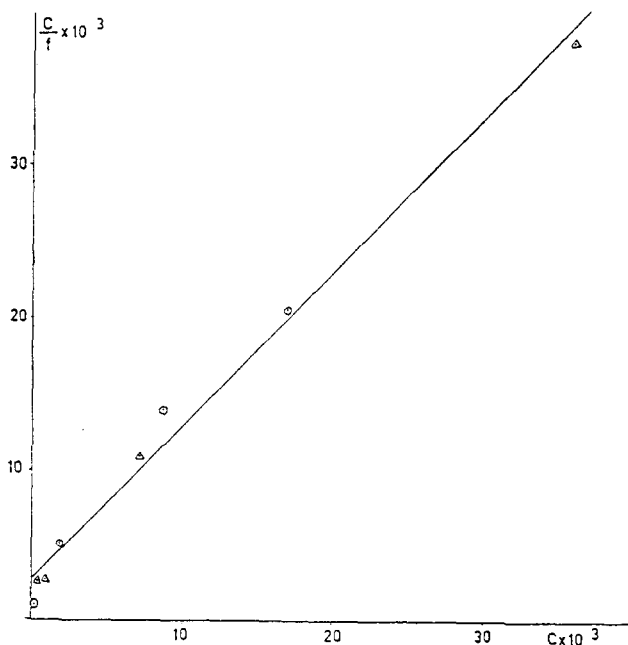
$$\frac{c}{f} = \frac{1}{k_t \tau} + c. \tag{9}$$

FIG. 4. Transfer efficiency as a function of benzophenone concentration for the system PVN-benzophenone excited with $\lambda = 3130$ Å at *LNT*. $\triangle$ and $\bigcirc$ correspond to two independent series of experiments.

Results are reported in Fig. 4 according to Eqn. (9) and a value of $k_t\tau$ of 40 l.mole^{-1} is obtained. As has been observed for polystyrene,[7,10] the life-time τ may be assumed to have the same value (30·2.10^{-9} sec) in the film as in solution.[7]

A k_t value of 1·3.10^9 l.mole^{-1} sec^{-1} is then obtained for transfer from PVN to benzophenone. This value is of the same order of magnitude as the rate constant obtained by Basile[11] for transfer from polystyrene to 1, 1, 4, 4, tetraphenylbutadiene (2·5.10^9 l.mole^{-1} sec^{-1}).

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(11) L. J. Basile, *Trans. Faraday Soc.* **60**, 1702 (1964).

Résumé—Le polyvinylnaphthalène ne donne lieu à aucune autre luminescence qu'une fluorescence d'excimère. L'absence de toute fluorescence ou phosphorescence normales suggère qu'il se produit une migration d'état singulet et une annihilation T.T. Le transfert d'énergie par état singulet du polyvinylnaphtalène solide à la benzophénone, à 77°K, est en accord avec la théorie de Förster sur les interactions dipole–dipole ($R_0 = 15$ Å). Dans les copolymères, l'efficacité du transfert d'unités vinylnaphtalène vers des unités vinylbenzophénone est un; on n'observe aucune phosphorescence ni pour la naphtalène ni pour la benzophénone.

Sommario—Nessuna altra luminescenza oltre alla fluorescenza per eccitazione può essere rilevata per il polivinilnaftalina. L'assenza di ogni fluorescenza o fosforescenza normale suggerisce la migrazione di un singoletto e la annichilazione T.T. L'energia di trasferimento del singoletto dal polivinilnaftalina solido al benzofenone a 77°K é in accordo con la teoria di Förster sull'interazione dipolo–dipolo ($R_0 = 15$ Å). Nei copolimeri l'efficienza del trasferimento dalla unità di vinilnaftalina a quella del vinilbenzofenone é unitaria; non é stata osservata né la fosforescenza della naftalina né quella del benzofenone.

Zusammenfassung—Für Polyvinylnaphthalin konnte außer einer Excimer Fluoreszenz keine andere Lumineszenz entdeckt werden. Die Abwesenheit von normaler Fluoreszenz oder Phosphoreszenz läßt eine Singulett Wanderung und T.T. Auslöschung vermuten. Ein Singulett Energietransfer vom festen Polyvinylnaphthalin auf Benzophenon bei 77°K steht in Übereinstimmung mit der Theorie von Förster für Dipol–Dipol Wechselwirkung ($R_0 = 15$ Å). In Copolymeren ist die Transferaktivität von Vinylnaphthalin auf Vinylbenzophenon-Einheiten gleich 1; weder eine Naphthalin noch eine Benzophenon Phosphoreszenz wurde beobachtet.