

ENERGY TRANSFER IN POLYMERS—VII

TRIPLET ENERGY MIGRATION AND TRANSFER IN COPOLYMERS STYRENE-VINYLBENZOPHENONE†

C. DAVID, V. NAEGELEN, W. PIRET and G. GEUSKENS

Faculté des Sciences, Université Libre de Bruxelles, B-1050 Brussels, Belgium

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Abstract—The efficiency of triplet energy transfer from the benzophenone group to naphthalene has been studied in a series of copolymers styrene-vinylbenzophenone, either as films or in glassy solutions at 77 K. Energy migration has been shown to be efficient in both cases. For a given copolymer, Hirayama's critical distance is larger in films than in glassy solutions. In both cases, it decreases with decreasing vinylbenzophenone content. The number of jumps between identical molecules during the life-time of the excited state has been calculated according to the hopping model and Voltz theory on energy migration. The results show that energy migration in these solid polymers is not the consequence of exchange interactions decreasing exponentially with the mean distance between the chromophores. Organized regions, characterized by a higher efficiency of transfer, have to be taken into account.

Excited triplet states of aliphatic and aromatic ketone groups are involved in the photodegradation of many polymers including polystyrene, polyethylene and polypropylene [1-3].

Therefore, a fundamental study of triplet energy migration is very important at 77 K in polyvinylbenzomatic and vinylaliphatic ketones was started a few years ago in our laboratory. It was shown, on the basis of energy transfer experiments, that energy migration is very important at 77 K in polyvinylbenzophenone (PVB) [4], and somewhat less in polyphenylvinylketone (PPVK) [5]. In polymethylvinylketone (PMVK) [6], it is negligible or non-existent. However, since the photodegradation of hydrocarbon polymers often involves only a few ketone groups present as impurities and distributed along the polymer chain, we have extended our study to the migration of energy between non-adjacent ketone groups in copolymers. In the present paper, the efficiency of energy transfer to naphthalene was measured for a series of copolymers styrene-

vinylbenzophenone as solid films and in glassy solutions in methyltetrahydrofuran at 77 K.

EXPERIMENTAL

The copolymers were obtained by Friedel-Crafts benzoylation of polystyrene using benzoylchloride and AlCl_3 in CS_2 . Their compositions (Table I) were determined by NMR in CDCl_3 and confirmed by absorption spectroscopy at λ_{max} of the first II-II* transition of the benzophenone chromophore. Dibenzoylation is quite unlikely because of both electronic and steric effects and could never be detected. Assuming the same ϵ at λ_{max} for benzophenone and for vinylbenzophenone units in the copolymer, the discrepancy between the two methods was less than 10%. The polymer films were cast under nitrogen from CH_2Cl_2 solutions. Identical results were obtained from benzene solutions. The experimental device for recording emission spectra of solid films has been previously described [7]. For glassy solutions at 77 K, an Hitachi-Perkin-Elmer MPF 2A fluorimeter equipped with the low temperature accessory was used. Identical emission spectra and transfer efficiency were obtained by excitation at 3340 and 3660 Å. The emission spectra were not corrected for the response of the photomultiplier.

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Table I. Phosphorescence of copolymers styrene-vinylbenzophenone energy transfer to naphthalene

Copolymer	Mole % VB	Films		Glassy solutions		
		O-O transition (Å)	R_0 (Å)	O-O transition (Å)	R_0 (Å)	$k_4\tau$ τ (l/mole)
2	0.7*	4170		4145		
3	1.6*	4200		4155		
4	9	4210	19.5	4160	11.9	17
6	15	4220	19.5	4170		
7	50	4260	23.5	4180	14.5	24
8	73	4280	27	4190	16.5	32
9	77	4290	31	4210	19	40

* Determined by u.v. absorption spectroscopy only.

RESULTS AND DISCUSSION

1. Emission spectra of the copolymers

The O-O transition of the phosphorescence of the copolymer films and glassy solutions at 77 K is given in Table 1. The whole spectrum is given in Fig. 1 for two of them. The emission spectra of the low benzophenone-content copolymers are very similar to that of benzophenone in a glass [12], and to the exciton phosphorescence of a pure crystal. In all cases, a red shift is observed in the phosphorescence spectrum as the vinylbenzophenone (VB) fraction increases. This shift is due to interactions between the benzophenone groups as supported by several data from the literature [8-10]. The O-O transition in the phosphorescence of polyvinylcarbazole is also reported by Klöpffer [8] to be shifted to the red when compared with a 500:1 styrene-vinylcarbazole copolymer. In the same way, the strong intermolecular interactions which occur at defect sites in crystalline benzophenone result in a red shift of the emission of crystals. According to recent papers, three types of T \rightarrow S emission are detected at 77 K in this case. Exciton phosphorescence has ν_{O-O} at $24,070\text{ cm}^{-1}$ (4150 Å) and a life time of 1.8×10^{-4} sec. Another spectrum beginning at $23,000\text{ cm}^{-1}$ (4350 Å) at 77 K is attributed by Rousset [9] to non-interacting molecules in vitreous domains formed as a consequence of defects inside the crystal: it is blue shifted when temperature is lowered from 77 to 7 K ($\nu_{O-O} = 24,100\text{ cm}^{-1}$ and $\tau = 2 \times 10^{-2}$ sec at 7 K). A last type of phosphorescence, with ν_{O-O} at $23,020\text{ cm}^{-1}$ (4345 Å) and $\tau = 4 \times 10^{-3}$ sec, the vibrational structure of which is similar to the exciton band but red shifted, is assigned by Offen *et al.* [10] to defects within the orthorhombic crystalline phase. This last emission

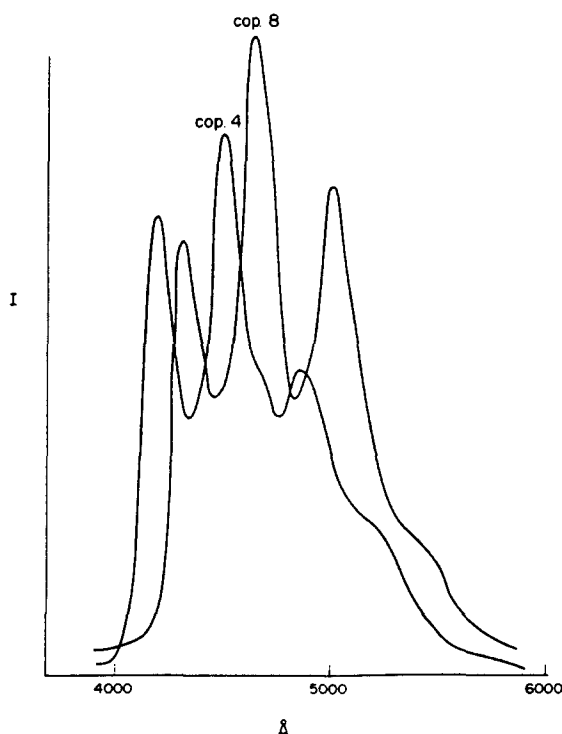


Fig. 1. Phosphorescence spectrum of styrene-vinylbenzophenone copolymer films at 77 K.

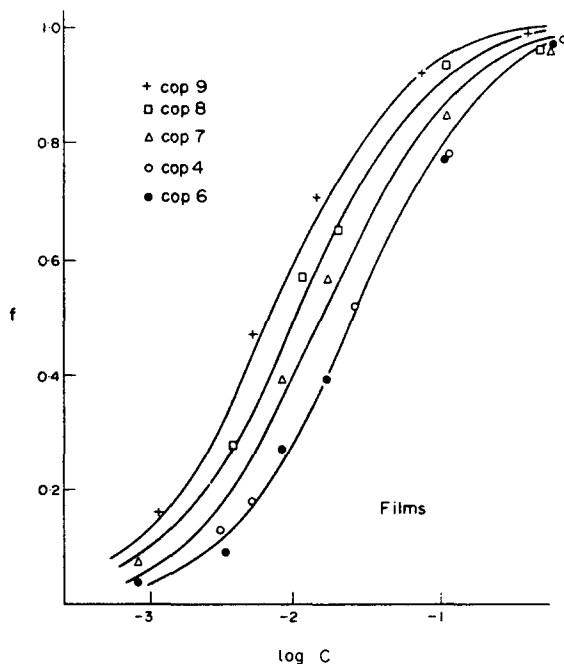


Fig. 2. Efficiency of transfer from vinylbenzophenone units to naphthalene in styrene-vinylbenzophenone copolymer films at 77 K.

replaces exciton phosphorescence when the crystal is subjected to pressure.

The progressive decrease in intensity of the third vibrational structure with decreasing VB contents in the copolymer films (Fig. 1) is due to a modification of the Franck-Condon potential energy surface owing to interactions between neighbouring groups.

2. Energy transfer to naphthalene

In the presence of increasing naphthalene concentration, the phosphorescence of benzophenone groups decrease and is progressively replaced by the phosphorescence of naphthalene. Absorption of the benzophenone phosphorescence by the long-lived triplet state of naphthalene ($\tau = 2.2$ sec) is possible since the T_1-T_2 transition in naphthalene is reported at 4150 Å [11]. This effect results in a deformation of the lowest energy vibrational structure of benzophenone as shown by Terenin and Ermolaev [12]. It has, however, been observed neither in films nor in solutions for the experimental conditions used in this work. Figures 2 and 3 give the efficiency of transfer as a function of naphthalene concentration for films and solutions of the various copolymers at 77 K. The efficiency of transfer f is defined as $(I_0 - I)/I_0$ where I_0 and I are, respectively, the emission intensity from VB measured at the maximum of the first vibrational structure in the absence and in the presence of naphthalene. For a given naphthalene concentration, f increases with VB contents in the copolymer. For a given copolymer and a given naphthalene concentration, it does not depend on the concentration of benzophenone units in the glassy solution. The importance of the migration can be characterized by the critical transfer distance of Hirayama [13], by the "hopping model" [14,15] or by the Stern-Volmer equation.

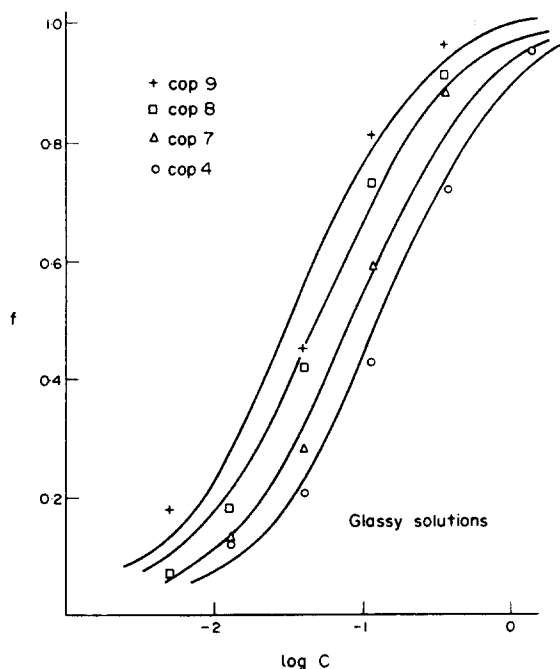


Fig. 3. Efficiency of transfer from vinylbenzophenone units to naphthalene in styrene-vinylbenzophenone copolymers in glassy solution at 77 K. ($C = 10^{-4}$ M/l in benzophenone groups.)

2.1 Hirayama's critical distance. The critical transfer distance R_0 defined by Hirayama [13] is the distance between a donor and an acceptor corresponding to an equal probability for exchange energy transfer and spontaneous deactivation in the absence of material diffusion or energy migration. R_0 is 12.9 Å for the transfer from benzophenone to naphthalene in a glassy solution at 77 K [13]. If the critical transfer distance determined in a solid polymer is larger than that value, it can be concluded that migration of energy is operative in that system. The R_0 values are thus useful for comparative purpose although such a treatment does not allow the quantitative evaluation of the photophysical processes responsible for the migration. It can be seen from Table 1 and Fig. 4 that in the copolymer with the highest mole fraction of VB, migration is very important since $R_0 = 31$ Å for the film and 19 Å for the glassy solution. Extrapolation of the results to 100% VB gives R_0 as 34 Å in the film, in agreement with the value previously published for polyvinylbenzophenone [4]. In the other copolymers R_0 decreases with VB contents. For copolymer 4 (9 mole % VB) in a glass, migration is negligible since R_0 is only 11.5 Å. In a film of the same copolymer, however, R_0 is 19 Å, indicating an efficient migration. As a general rule for any copolymer, R_0 is lower in a glassy solution than in a film. This effect will be discussed later.

2.2 Hopping model and Stern-Volmer equation. The "hopping model" frequently used for the study of energy transfer in mixed crystals and the Stern-Volmer equation are strictly valid only when migration is so important that a statistical mixing of donor and acceptor groups occurs during the lifetime of the donor.

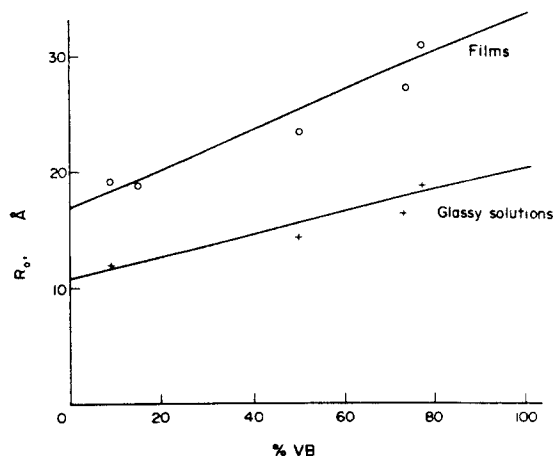
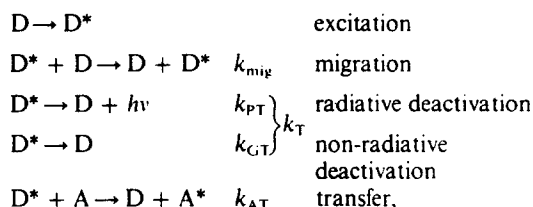


Fig. 4. Critical transfer distance to naphthalene at 77 K as a function of vinylbenzophenone content in styrene-vinylbenzophenone copolymers.

Considering the simple scheme



and assuming a stationary state for the excited states:

$$\frac{I_0}{I} = 1 + \frac{k_{\text{AT}}}{k_{\text{T}}} [A] = 1 + k_{\text{AT}} \tau [A], \quad (1)$$

where I_0 and I are the emission intensity from the donor in the absence and in the presence of acceptor, respectively. Equation (1) is the usual form of the Stern-Volmer equation. In the "hopping model" excitation is assumed to migrate by jumping from one donor group to another. The Stern-Volmer equation can be written as

$$\frac{I_0}{I} - 1 = Q = k_{\text{AT}} \tau [A]. \quad (2)$$

On the other hand, it can be assumed that:

$$(1 - p) k_{\text{mig}} = k_{\text{AT}},$$

where p is the probability for the exciton to return to its starting point. It has been shown that $(1 - p)$ is 0.66 for a random walk in three dimensions [16,17]. The number of jumps from D^* to D per unit time is $k'_{\text{mig}} = k_{\text{mig}} [D]$. This gives:

$$Q = (1 - p) k'_{\text{mig}} \tau \frac{[A]}{[D]}.$$

This equation is the usual expression of the "hopping model". If Q is plotted as a function of $[A]/[D]$, $k'_{\text{mig}} \tau$, the number of jumps during the life time of the excited state, can be obtained from the slope of the straight line. An independent measurement of τ allows the number of jumps per unit time to be determined. The "hopping model" cannot be used for glassy solutions of polymers since $[D]/[A]$ in the coil cannot

Table 2. Triplet energy transfer to naphthalene in styrene-vinylbenzophenone copolymer films

Copolymer	[D] mole l ⁻¹	$k'_{\text{mig}} \tau^*$	$R(\text{\AA})^\dagger$	$\bar{r}(\text{\AA})^\ddagger$	$e - 2R/1.35\bar{r}$
4	0.75	43	16.5	108	$2.42 \cdot 10^{-11}$
6	1.19	71	13.6	115	$1.78 \cdot 10^{-9}$
7	3.21	211	10	145	$3.68 \cdot 10^{-7}$
8	4.12	692	9.2	242	$1.20 \cdot 10^{-6}$
9	4.17	1013	9.1	290	$1.40 \cdot 10^{-6}$

* Number of jumps during the life time of the excited state.

† Mean distance between benzophenone groups.

‡ Mean displacement of excitation during the life time of the excited state.

§ $1.35 \text{\AA} = L =$ mean effective Bohr radius.

be calculated. In that case, the Stern-Volmer equation should be used. The values of $k'_{\text{mig}} \tau$ obtained for solid films of the copolymers styrene-vinylbenzophenone are given in Table 2.

The mean displacement of excitation during the life time of the excited state calculated according to:

$$\bar{r} = R_0(k'_{\text{mig}} \tau)^{1/2},$$

where R is the mean distance between VB groups in the copolymers, is also given in Table 2. If energy migration occurs by exchange interaction between identical molecules, the number of jumps per unit time can be interpreted according the Robinson-Frosch [17] theory for weak coupling interactions between identical molecules. In that case the initial state is that where the first molecule (s) is electronically excited and the other (s') in the ground state. In the final state, the second molecule is excited and the first is in its ground state. Transition between the initial and the final state occurs in an average time

$$t_{\text{avg}} = h/4uS^2,$$

where S is of the overlap integral of the vibrational eigenfunctions of the ground state S_0 and first triplet state T_1 and

$$u = \int \psi_1^*(s) \psi_0^*(s') V(s, s') \psi_0(s) \psi_1(s') d\tau(s) d\tau(s').$$

$V(s, s')$ is in this case the operator of exchange interactions. The value of u for exchange interactions is related to the factor Z defined by Dexter [18] and Hirayama [13]. It decreases exponentially with R since electronic wave functions of a molecule generally decline exponentially. In agreement with the theory of Dexter and Hirayama, it can thus be written that

$$u = K e^{-2R/L},$$

where K is a proportionality constant, L is the "effective average Bohr radius" = 1.35\AA . In the case of migration, transfer occurs between identical molecules and thus D and A both represent benzophenone groups. If the life time is supposed to be independent of copolymer composition, the number of jumps per unit time may be expected to vary as:

$$k'_{\text{mig}} \tau = K' \exp(-2R/L),$$

where K' is a constant.

Examination of Table 2 shows that the number of jumps during the life time of the excited state for

copolymer 4 is lower by a factor of 20 than $k'_{\text{mig}} \tau$ for copolymer 9, whereas the exponential term is reduced by a factor of 6×10^4 . Agreement between these values would require that τ differs by a factor of 3×10^3 for copolymers 4 and 9. Direct measurements of the life time in our laboratory have recently shown that they actually differ by a factor of less than 3. The constant k'_{mig} thus depends on the composition of copolymers but less than would be expected from the Dexter relation. It should be mentioned that the number of jumps during the life time can also be obtained from the theory of Voltz [19] which was applied previously to PVB [4] and is more elaborate than the "hopping model". A factor of 20 is also obtained between copolymers 4 and 9 in that case.

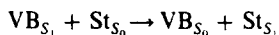
In glassy solutions of copolymers, the Stern-Volmer equation can be applied to our results (Table 1). If the phosphorescence life time is of the order of 5×10^{-3} sec as for benzophenone in a glass, k_{AT} is 6×10^3 l/mole/sec for copolymer 8.

2.3. *The mechanism of energy migration.* Our results indicate that energy migration is important in films and glassy solutions of styrene-vinylbenzophenone copolymers. Comparative study of the copolymer films shows that it is not the consequence of exchange transfer between identical groups which should decrease exponentially with the mean distance between chromophores. These results can be compared with other data in the literature and the various processes that could be responsible for energy migration can be discussed.

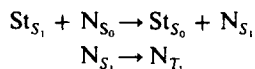
In glassy solutions, the transfer to naphthalene is characterized by $k_{\text{AT}} \tau = 32$ l/mole for copolymer 8, whereas a value of 50 l/mole is obtained for polycenaphthylene [20] and polyvinyl naphthalene [21] and a value of 1500 [22] in the case of transfer from polystyrene to perylene. This corresponds respectively to $k_{\text{AT}} = 6 \times 10^3$, 40 and 5×10^2 l/mole/sec since τ values are respectively 5×10^{-3} sec (copolymer 8), 1.25 sec (polyvinyl naphthalene and polycenaphthylene) and 3 sec (polystyrene). Energy migration was found to be efficient in a glassy solution of polyphenylvinylketone but negligible in polymethylvinylketone (23). It can thus be important in glassy solution, although less than in films. Since migration can occur even in dilute glassy solution, it is to be assigned in that case to intramolecular interaction in the polymer coil. The efficiency of transfer is indeed independent of the polymer concentrations in glassy solutions of copolymers styrene-vinylbenzophenone.

In the case of films, two problems have to be considered: the mechanism of energy migration in (St-VB) copolymers; the relative importance of the migration in the solid polymers so far studied.

Participation of the styrene units in photophysical processes possibly responsible for migration in the copolymers St-VB has to be considered. Energy transfer

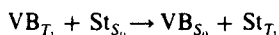


followed by



is improbable owing to the high rate of inter-system crossing in aromatic ketones.

A second process



would require thermal activation of VB triplet to a higher vibrational level. Since polystyrene is not phosphorescent, the O-O transition is not known. It is $28,900 \text{ cm}^{-1}$ (3460 \AA) for toluene, but luminescence study of other styrene copolymers has shown that the first vibrational structure of the phosphorescence has in this case a maximum at $3900\text{--}3950 \text{ \AA}$ [24]. The problem of temperature-dependent reversible transfer has been treated by Hirota [25] and Lamola [26]. The position of the equilibrium depends on the energy difference between the triplet state and on the value of the rate constants for the various photophysical processes of deactivation, migration and transfer. On the basis of their results, triplet transfer to the matrix cannot be excluded. However, in this case, the phosphorescence of the styrene units would have to appear as the temperature is raised. This is not observed. Participation of the matrix to singlet or triplet energy transfer has thus a very low probability. As a conclusion, it can be assumed that organized regions in copolymers are characterized by a higher efficiency of energy migration than expected from exchange interactions. The existence of such organized regions in films justifies the difference of transfer efficiency observed for a given copolymer between a film and a glassy solution. In this latter case, indeed, such an organization does not exist at low concentration when the macromolecules can be considered as isolated.

The values of R_0 reported in the literature for triplet transfer in solid polymers can now be compared. The range of R_0 for the copolymers styrene-vinylbenzophenone varies from 20 to 34 \AA with benzophenone content; values of 26 and 11 \AA were measured previously for PPVK and PMVK. All these polymers are characterized by a short phosphorescence life time due to emission from a $n\text{--}\Pi^*$ transition. From data reported by Klöppfer, the R_0 value for transfer from the long-lived $\Pi\text{--}\Pi^*$ triplet state of polyvinyl-carbazole can be estimated as between 35 and 45 \AA while it is 15 \AA for polystyrene [27]. This indicates that the importance of migration is not directly related

to the life time of the excited state. If the efficiency of transfer in polymers is now compared with that of the model compound in the crystalline form, it can be concluded that triplet migration is more important in the crystal than in the polymer. It can be inferred that efficient triplet traps are formed on destroying the three-dimensional order of the crystal.

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Résumé—Le transfert d'énergie triplet du groupe benzophénone au naphthalène a été étudié dans une série de copolymères styrène-vinylbenzophénone soit sous forme de films, soit en solution vitreuse à 77 K. Une importante migration d'énergie a été mise en évidence dans les deux cas. Pour un copo-

lymère donné, la distance critique de transfert définie par Hirayama est plus grande pour les films que pour les solutions vitreuses. Dans les deux cas, elle diminue avec la teneur en benzophénone. Le nombre de sauts entre molécules semblables pendant la durée de vie de l'état excité a été calculé selon le "hopping model", et selon la théorie de Voltz. Les résultats montrent que la migration d'énergie dans les films n'est pas le résultat d'interactions d'échange diminuant exponentiellement avec la distance moyenne entre les chromophores benzophénone. L'existence dans ces polymères de régions organisées caractérisées par une plus grande efficacité de transfert doit être prise en considération.